A

SYSTEM OF INSTRUCTION

IN

QUALITATIVE CHEMICAL ANALYSIS.

In the Press,

BY THE SAME AUTHOR.

QUANTITATIVE CHEMICAL ANALYSIS.

Third Edition. 8vo. cloth.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS.

BY

Karl

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Fifth Edition.

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EDITOR'S PREFACE

TO THE

FIFTH EDITION.

THIS Edition of Dr. Fresenius's Qualitative Chemical Analysis, though simply professing to be a translation from the NINTH GERMAN Edition, is really very much in advance of that work; it contains a large amount of important original matter communicated by the Author during the time it was passing through the press. Some of the sections have also been remodelled, to adapt them to the more advanced state of scientific instruction.

It is very gratifying to the Editor to find that, notwithstanding the numerous and important English works on chemical analysis published within the last few years, the valuable system of Dr. Fresenius still enjoys the undiminished confidence of British chemists.

In conclusion, the Editor expresses a hope that the present edition will receive the same amount of favor as the former works of the distinguished Author.

J. LLOYD BULLOCK.

3, HANOVER STREET, W.
October, 1859.

EDITOR'S PREFACE.

This work of Dr. Fresenius has already gone through two editions in Germany. The abundant opportunities enjoyed by its Author of discovering the wants felt by students in entering upon the practice of chemical analysis, and his position in the School of Giessen, have enabled him to devise a method of study of the highest value. That it has received the approbation of the illustrious HEAD of that school, and the benefit of three years' practical experience under his immediate observation, must powerfully recommend it to the English student of chemistry. Whoever is desirous of obtaining the knowledge necessary to become a practical chemist, will be in no small degree indebted to Dr. Fresenius for the facilities thus afforded him. Every one who knows anything of Giessen, will bear testimony to the rigid economy of time, and the resolute adoption of every improvement in method which characterize that school, and serve to accomplish the many chemists annually flocking there for the completion of their studies. The Author, in his Preface to the First Edition, tells us that he was led to compose this volume upon perceiving that the larger works on chemical analysis, such as H. Rose's, Duflos's, and others, although admirable in themselves, present great difficulties to beginners, which difficulties may be summed up under three heads; 1st, Too great copiousness and detail; 2nd, The absence of explanations of the causes of phenomena, *i. e.* the *theory* of the operations and reactions; and 3rd, The omission altogether of many substances

of very frequent occurrence, especially in the operations of the pharmaceutist, such as the organic acids, &c.

In avoiding these objections to former works on chemical analysis, Dr. Fresenius, I think, is not chargeable with having fallen into the opposite extreme of being too concise or elementary.

The student may, perhaps, at first be disappointed in taking up this work to find that there are no tables constructed to furnish him at a glance with all he is desirous to know of tests and reactions, and to save him, as he may think, trouble and time. But this has not arisen from oversight; the question of the advantage or disadvantage of tables to the student has been fully considered, and the Author has decided—and the decision is borne out by the highest authorities—that such tables serve no really good purpose; they rather, on the contrary, supply but very superficial information, and satisfy the student before they have really informed him. The information contained in this work, like every other professing to teach a practical science, requires application and perseverance to attain; but if begun at the beginning, if the student will carefully go over the necessary preliminary facts, the examination of his tests, and the reaction of the simple bodies consecutively, and make himself master of this very simple and elementary part of the course, he will find few or no difficulties when entering upon the more elaborate, and—what might appear, without this preparation—complex and intricate processes of the Second Part, the analysis of compound bodies. It is altogether another question whether the student should or should not exercise himself and his memory by tabulating the results of his experiments as he proceeds; and to this question we reply in the affirmative; but it must be left to individuals to act in this according to their own judgment, and their own feeling of its necessity.

In the Preface to the Second Edition, Dr. Fresenius tells us that his work has met with much success, having been adopted in the Pharmaceutical Institution of Bonn, &c., as well as in the laboratory of Giessen; and that he has improved it by many corrections and additions.

For my own part, I may be allowed to observe that the English Edition was undertaken by the express desire of Professor Liebig, who kindly recommended its being intrusted to my care. The Author has supplied me with many corrections, and some additions, and the hope is shared by us in common that it will facilitate the study of analytical chemistry to the English student, and in every way serve to promote the interests of the science.

J. LLOYD BULLOCK.

22, Conduit Street,
October 1, 1843.

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PART I.

INTRODUCTORY.

PRELIMINARY REMARKS.

DEFINITION, GENERAL PRINCIPLES, OBJECTS, UTILITY, AND IMPORTANCE OF QUALITATIVE CHEMICAL ANALYSIS, THE CONDITIONS AND REQUIREMENTS FOR A SUCCESSFUL STUDY OF THAT SCIENCE.

CHEMISTRY is the science which treats of the various materials entering into the structure of the earth, their composition and decomposition, their mutual relations and deportment in general. A special branch of this science is designated *Analytical Chemistry*, inasmuch as it pursues a distinct and definite object—viz., the analysis of compound bodies, and the examination of their component elements. Analytical chemistry, again, is subdivided into two branches—viz., *qualitative analysis*, which simply studies the *nature* and properties of the component parts of bodies; and *quantitative analysis*, which ascertains the *quantity* of every individual element present. The office of qualitative analysis, therefore, is to exhibit the constituent parts of a substance of *unknown* composition in forms of *known* composition, from which the constitution of the body examined, and the presence of its several component elements may be positively inferred. The efficiency of its method depends upon two conditions—viz., it must attain the object in view with unerring certainty, and in the most expeditious manner. The object of quantitative analysis, on the other hand, is to exhibit the elements revealed by the qualitative investigation in forms which will permit the most accurate estimate of their weight, or to effect by other means the determination of their quantity.

These different ends are, of course, attained respectively by very different ways and means. The study of qualitative analysis must, therefore, be pursued separately from that of quantitative analysis, and must naturally precede it.

Having thus generally defined the meaning and scope of qualitative analysis, we have now still to consider, in the first place, the preliminary information required to qualify students for a successful cultivation of this branch of science, the rank which it holds in the domain of chemistry, the bodies that fall within the sphere of its operations, and its utility and importance; and, in the second place, the principal parts into which its study is divided.

It is, above all, absolutely indispensable for a successful pursuit of qualitative investigations, that the student should possess some knowledge of the chemical *elements*, and of their most important combinations, as well as of the principles of chemistry in general; and that he should combine with this knowledge some readiness in the apprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student joins to these qualifications the habit of invariably ascribing the failures with which he may happen to meet, to some error or defect in his operations, or, in other words, to the absence of some condition or other indispensable to the success of the experiment—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit —he possesses every requisite to render his study of analytical chemistry successful.

Now, although chemical analysis is based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we have to look upon it as one of the main pillars upon which the entire structure of the science rests; since it is of almost equal importance for all branches of theoretical as well as of practical chemistry; and I need not expatiate here on the advantages which the physician, the pharmaceutist, the mineralogist, the rational farmer, the manufacturer, the artisan, and many others derive from it.

This consideration would surely in itself be sufficient reason to recommend a thorough and diligent study of this branch of science, even if its cultivation lacked those attractions which yet it unquestionably possesses for every one who devotes himself zealously and ardently to it. The human mind is constantly striving for the attainment of truth; it delights in the solution of problems; and where do we meet with a greater variety of them, more or less difficult of solution, than in the province of chemistry? but as a problem to which, after long pondering, we fail to discover the key, wearies and discourages the mind: so, in like manner, do chemical investigations, if the object in view is not attained—if the results do not bear the stamp of truth, of unerring certainty. A *half-knowledge* is therefore, as indeed in every department of science, but more especially *here*, to be considered worse than no knowledge at all; and a mere *superficial* cultivation of chemical analysis is consequently to be particularly guarded against.

A qualitative investigation may be made with a twofold view—viz., either, 1st, to prove that a certain body is or is not contained in a substance, *e.g.* lead in wine; or, 2nd, to ascertain *all* the constituents of a chemical compound or mixture. Any substance whatever may of course become the object of a chemical analysis.

In the present work, however, we purpose to confine ourselves to those elements and compounds which are more generally employed in pharmacy, in the arts and manufactures, and in agriculture.

The study of qualitative analysis is most properly divided into four principal parts—viz.,

1. Chemical operations.
2. Reagents and their uses.
3. Deportment of the various bodies with reagents.
4. Systematic course of qualitative analysis.

It will now be readily understood that the pursuit of chemical

analysis requires *practical skill and ability*, as well as *theoretical knowledge;* and that, consequently, a mere speculative study of that science can be as little expected to lead to success as purely empirical experiments. To attain the desired end, theory and practice must be combined.

SECTION I.

OPERATIONS.

§ 1.

THE operations of analytical chemistry are essentially the same as those of synthetical chemistry, though modified to a certain extent to adapt them to the different object in view, and to the small quantities operated upon in analytical investigations.

The following are the principal operations in qualitative analysis.

§ 2.

1. SOLUTION.

The term "*solution*," in its widest sense, denotes the perfect union of a body, no matter whether gaseous, liquid, or solid, with a fluid, resulting in a homogeneous liquid. However, when the substance dissolved is *gaseous*, the term "*absorption*" is more properly made use of; and the solution of one fluid in another is more generally called a *mixture*. The application of the term solution, in its usual and more restricted sense, is confined to the perfect union of a *solid* body with a fluid.

A solution is the more readily effected the more minutely the body to be dissolved is divided. The fluid by means of which the solution is effected, is called the *solvent*. We call the solution *chemical*, where the solvent enters into chemical combination with the substance dissolved; *simple*, where no definite combination takes place.

In a *simple* solution the dissolved body exists in the free state, and retains all its original properties, except those dependent on its form and cohesion; it separates unaltered when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt in this case imparts its peculiar taste to the fluid. On evaporating the water, the salt is left behind in its original form. A simple solution is called *saturated* when the solvent has received as much as it can hold of the dissolved substance. But as fluids dissolve generally larger quantities of a substance, the higher their temperature, the term *saturated*, as applied to *simple* solutions, is only relative, and refers invariably to a certain temperature. It may be laid down as a general rule, that elevation of temperature facilitates and accelerates simple solution.

A *chemical* solution contains the dissolved substance not in the same state nor possessed of the same properties as before; the dissolved body is no longer free, but intimately combined with the solvent, which latter also has lost its original properties; a new substance has thus been produced, and the solution manifests therefore now the properties of this new substance. A chemical solution also may be *accelerated* by elevation of temperature; and this is indeed usually the case, since heat generally

promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference of temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature.

The reason of this is, that in a chemical solution the solvent and the body upon which it acts have invariably opposite properties, which they strive mutually to neutralize. Further solution ceases as soon as this tendency of mutual neutralization is satisfied. The solution is in this case also said to be saturated or, more properly, *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization. The substances which produce chemical solutions are, in most cases, either acids or alkalies. With few exceptions, they have first to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present; *e.g.* when solution of acetic acid in water is brought into contact with oxide of lead, there ensues, first, a chemical combination of the acid with the oxide, and then a simple solution of the new-formed acetate of lead in the water of the menstruum.

In pharmacy, solutions are often made in a mortar having a lip, by triturating the body to be dissolved with the solvent added gradually in small quantities at a time; in chemical laboratories solutions are rarely made in this manner, but generally by digesting or heating the substance to be dissolved with the fluid in beaker-glasses, flasks, test-tubes, or dishes. In the preparation of chemical solutions, the best way generally is to mix the body to be dissolved in the first place with water (or with whatever other indifferent fluid may happen to be used), and then gradually add the chemical agent. By this course of proceeding a large excess of the latter is avoided, an over-energetic action guarded against, the process greatly facilitated, and complete solution ensured, which is a matter of some importance, as it will not seldom happen in chemical combinations that the product formed refuses to dissolve if an excess of the chemical solvent is present; in which case the molecules first formed of the new salt, being insoluble in the menstruum present, gather round and enclose the portion still unacted on, weakening thereby or preventing altogether further chemical action upon them. Thus, for instance, Witherite (carbonate of baryta) dissolves readily when, after being reduced to powder, water is poured upon it, and hydrochloric acid gradually added; but it dissolves with difficulty and imperfectly when projected into a concentrated solution of hydrochloric acid in water, for chloride of barium will indeed dissolve in water, but not in hydrochloric acid.

CRYSTALLIZATION and PRECIPITATION are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both generally depend on the same cause, viz., on the absence of a solvent, it is impossible to assign exact limits to either; in many cases they merge into one another. We must, however, consider them separately here, as they differ essentially in their extreme forms, and as the special objects which we purpose to attain by their application are generally very different.

§ 3.

2. Crystallization.

We understand by the term crystallization, in a more general sense, every operation, or process, whereby bodies are made to pass from the fluid to the solid state, and to assume certain fixed, mathematically definable, regular forms. But as these forms, which we call *crystals*, are the more regular, and consequently the more perfect, the more slowly the operation is carried on, we always connect with the term "crystallization" the accessory idea of a *slow* separation—of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangement of the ultimate constituent particles of bodies (*molecules* or *atoms*); it can only take place, therefore, if these atoms possess perfect freedom of motion, and thus in general only when a substance passes from the fluid or gaseous to the solid state. Those instances in which the mere ignition, or the softening or moistening of a solid body, suffices to make the tendency of the molecules to a regular arrangement (crystallization) prevail over the diminished force of cohesion—such as, for instance, the turning white and opaque of moistened barley-sugar—are to be regarded as exceptional cases.

To induce crystallization, the causes of the fluid or gaseous form of a substance must be removed. These causes are either *heat alone, e.g.*, in the case of fused metals; or *solvents alone*, as in the case of an aqueous solution of common salt; or *both combined*, as in the case of a hot saturated solution of nitrate of potassa in water. In the first case we obtain crystals by cooling the fused mass; in the second, by evaporating the menstruum; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of the crystals are called *mother-waters*, or *mother-liquors*. The term *amorphous* is applied to such solid bodies as have no crystalline form.

We have recourse to crystallization generally either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum. In many cases also the form of the crystals or their deportment in the air, viz., whether they remain unaltered or effloresce, or deliquesce, upon exposure to the air, will afford an excellent means of distinguishing between bodies otherwise resembling each other; for instance, between sulphate of soda and sulphate of potassa. The process of crystallization is usually effected in dishes, or, in the case of very small quantities, in watch-glasses.

In cases where the quantity of fluid to be operated upon is only small, the surest way of getting well-formed crystals is to let the fluid evaporate in the air, or, better still, under a bell-glass, with an open vessel half-filled with concentrated sulphuric acid. Minute crystals are examined best with a lens, or under the microscope.

§ 4.

3. Precipitation.

This operation differs from the preceding one in this much, that the dissolved body is converted to the solid state, not slowly and gradually,

but *suddenly*, no matter whether the substance separating is crystalline or amorphous, whether it sinks to the bottom of the vessel, or ascends, or remains suspended in the liquid. Precipitation is either caused by a modification of the solvent—thus sulphate of lime (gypsum) separates immediately from its solution in water upon the addition of alcohol; or it ensues in consequence of the separation of an educt insoluble in the menstruum—thus when ammonia is added to a solution of sulphate of alumina, the latter salt is decomposed, and the alumina, not being soluble in water, precipitates. Precipitation takes place also when, by the action of simple or double chemical affinity, new compounds are formed which are insoluble in the menstruum; thus oxalate of lime precipitates upon adding oxalic acid to a solution of acetate of lime; chromate of lead upon mixing chromate of potassa with nitrate of lead. In decompositions of this kind, induced by simple or double affinity, one of the new compounds remains generally in solution, and the same is sometimes the case also with the educt; thus in the instances just mentioned the sulphate of ammonia, the acetic acid, and the nitrate of potassa, remain in solution. It may, however, happen also that both the product and the educt, or two products, precipitate, and that nothing remains in solution; this is the case, for instance, when a solution of sulphate of magnesia is mixed with water of baryta, or when a solution of sulphate of silver is precipitated with chloride of barium.

Precipitation is resorted to for the same purposes as crystallization, viz., either to obtain a substance in the solid form, or to separate it from other substances dissolved in the same menstruum. But in qualitative analysis we have recourse to this operation more particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment which they exhibit when precipitated either in an isolated state or in combination with other substances. The solid body separated by this process is called the *precipitate*, and the substance which acts as the immediate cause of the separation is termed the *precipitant*. Various terms are applied to precipitates by way of particularizing them according to their different nature; thus we distinguish crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, &c.

The terms *turbid*, *turbidity*, are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. The separation of flocculent precipitates may generally be promoted by a vigorous shake of the vessel; that of crystalline precipitates, by stirring the fluid, and rubbing the sides of the vessel with a glass rod; elevation of temperature is also an effective means of promoting the separation of most precipitates. The process is therefore conducted, according to circumstances, either in test-tubes, flasks, or beakers.

The two operations described respectively in §§ 5 and 6, viz., *filtration* and *decantation*, serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. Filtration.

This operation consists simply in passing the fluid from which we wish to remove the solid particles mechanically suspended therein through a

filtering apparatus, formed usually by a properly arranged piece of unsized paper placed in a funnel; an apparatus of this description allows the fluid to trickle through with ease, whilst it completely retains the solid particles. We employ smooth filters and plaited filters; the former in cases where the separated solid substance is to be made use of, the latter in cases where it is simply intended to clear the solution. Smooth filters are prepared by double-folding a circular piece of paper, with the folds at right angles; they must in every part fit close to the funnel. The preparation of plaited filters is more properly a matter for ocular demonstration than for description. In cases where the contents of the filter require washing, the paper must not project over the rim of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but also renders the solid particles less liable to be carried through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially such as are dissolved by acids, *e.g.*, sesquioxide of iron and lime. The common filtering paper of commerce seldom comes up to our wants in this respect, and I would therefore always recommend to wash it carefully with dilute hydrochloric acid whenever it is intended for use in *accurate analyses.* With the stronger sorts of paper this may be done by placing the paper cut in circular discs, in a layer of moderate thickness, in a shallow porcelain dish, pouring over it a mixture of one part of hydrochloric acid or nitric acid with about nine parts of water, and letting it digest for several hours at a moderate heat. The fluid is then poured off, and the paper repeatedly washed with water (finally with distilled water), until litmus paper is no longer reddened by the washings: the water is then drained off, and the entire layer is carefully transferred to a quire of blotting-paper, and left there until they can be taken off singly without injury; they are then hung up to dry on lines in a place free from dust. With the finer sorts of paper (Swedish paper) I prefer washing the filters in the funnel. To this end they are first sprinkled with a little moderately diluted hydrochloric or nitric acid, and then thoroughly washed with water, finally with distilled water. Filtering paper, to be considered good, must, besides being pure, also let fluids pass readily through, whilst yet completely retaining even the finest pulverulent precipitates, such as sulphate of baryta, oxalate of lime, &c. If a paper satisfying these requirements cannot be readily procured, it is advisable to keep two sorts, one of greater density for the separation of very finely divided precipitates, and one of greater porosity for the speedy separation of grosser particles. The funnels must be of glass or porcelain (§ 14, 10); they are usually placed on an appropriate stand, to keep them in a fixed position. The stand shown in Fig. 1 is particularly well adapted for the reception of the small-sized funnels used in qualitative analyses.

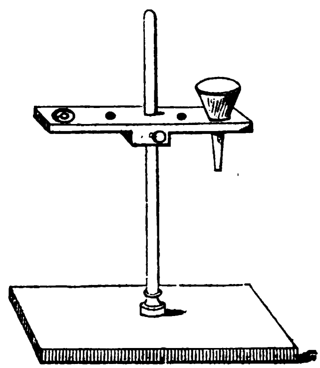


Fig. 1.

§ 6.

5. Decantation.

This operation is frequently resorted to instead of filtration, in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; as they will in such cases speedily subside to the bottom, thereby rendering it easy either to decant the supernatant fluid by simply inclining the vessel, or to draw it off by means of a syphon or pipette.

In cases where filtration or decantation are resorted to for the purpose of obtaining the solid substance, the latter has to be freed afterwards by repeated washing from the liquid still adhering to it. This operation is termed *washing* or *edulcoration*. The washing of precipitates collected on a filter is usually effected by means of a washing bottle, such as is shown in Fig. 2.

Fig. 2.

Fig. 3.

This washing bottle consists of a flask closed with a perforated cork, into which a small glass tube is fitted, with the outer end drawn out to a fine point. By blowing air into the flask through this tube and, when the air is sufficiently compressed, reversing the flask, so as to place the inner aperture of the tube under water, a fine jet of that fluid is expelled with a certain degree of force; this contrivance is well adapted for washing precipitates. Fig. 3 represents a washing bottle of a different construction, which is used more especially to wash precipitates with boiling water, and affords also the advantage that it enables the operator to produce an uninterrupted jet of water. The drawing needs no explanation; the outer end of the tube *a* is drawn out to a fine point. An India-rubber cap fitted with two tubes may be used instead of the double-perforated cork.

There are four operations which serve to separate volatile substances from less volatile or from fixed bodies, viz., *evaporation*, *distillation*, *ignition*, and *sublimation*. The two former of these operations are applied exclusively to fluids, the two latter exclusively to solids.

§ 7.

6. Evaporation.

This operation is of very frequent occurrence. It serves to separate volatile fluids from less volatile or from fixed bodies (no matter whether solid or fluid), in cases where the residuary substance alone is of importance, whilst the evaporating matter is entirely disregarded;—thus, for instance, we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to bring about crystallization of the salt; we resort to this process also for the purpose of removing the whole of the water of the menstruum from the solution of a non-crystallizable substance, so as to obtain the latter in a solid form, &c. The evaporated water is entirely disregarded in either of these cases, the only object in view being to obtain, in the former case a more concentrated fluid, and in the latter a dry substance. These objects are invariably attained by converting the fluid which is to be removed to the gaseous state. This is generally done by the application of heat; sometimes also by leaving the fluid for a certain time in contact with the atmosphere, or with an enclosed volume of air constantly kept dry by hygroscopic substances, such as concentrated sulphuric acid, chloride of calcium, &c.; or, lastly, in many cases, by placing the fluid in rarefied air, with simultaneous application of hygroscopic substances. As it is of the utmost importance in qualitative analyses to guard against the least contamination, and as an evaporating fluid is the more liable to this the longer the operation lasts, the process is usually conducted, with proper expedition, over the flame of a spirit or gas-lamp, in a separate place free from dust and not exposed to draughts of air. If the operator has no place of the kind, he must have recourse to the much less suitable proceeding of covering the dish; the best way of doing this is to place over the dish a large glass funnel secured by a retort holder, in a manner to leave sufficient space between the rim of the funnel and the border of the dish; the funnel is placed slightly aslant that the drops running down its sides may be received in a beaker. Or the dish may also be covered with a sheet of filter paper previously freed from inorganic substances by washing with dilute hydrochloric or nitric acid (see § 5); were common and unwashed filter paper used for the purpose, the sesquioxide of iron, lime, &c., contained in it, would dissolve in the vapors evolved (more especially if acid), and the solution dripping down into the evaporating fluid would speedily contaminate it. These precautions are necessary of course only in accurate analyses. Larger quantities of fluid are evaporated best in glass flasks standing aslant, covered with a cap of pure filtering paper, over a charcoal fire or gas; or also in retorts. Evaporating processes at 212° are conducted in an appropriate steam apparatus, or in the water-baths shown in Fig. 4.

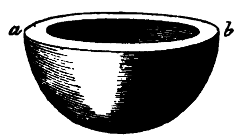


Fig. 4.

§ 8.

7. Distillation.

This operation serves to separate a volatile liquid from a less volatile

or a fixed substance (no matter whether solid or fluid), where the object is to recover the evaporating fluid. In order to attain this object, it is necessary to reconvert the liquid from the gaseous form in which it evaporates, into the fluid state. A distilling apparatus consists consequently always of three parts, no matter whether admitting of separation or not. These three parts are—1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor; 2nd, an apparatus in which this vapor is cooled again or *condensed*, and thus reconverted to the fluid state; and 3rd, a vessel to receive the fluid thus reproduced by the condensation of the vapor (the distillate). For the distillation of large

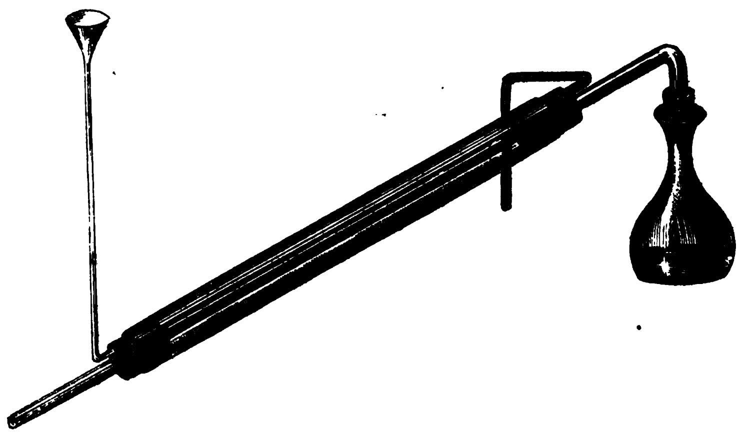


Fig. 5.

quantities we use either a metallic apparatus (a copper still with head and condenser made of tin or pewter), or large glass retorts; in analytical investigations we generally employ the apparatus shown in Fig. 5.

§ 9.

8. Ignition.

Ignition is, in a certain measure, for solid bodies what evaporation is with regard to fluids; since it serves (at least generally) to separate volatile substances from less volatile or from fixed bodies, in cases where the residuary substance alone is of importance. The process of ignition always presupposes the application of a high temperature, in which it differs from that of drying or exsiccation. The form or state which the eliminated substance assumes on cooling—whether it remains gaseous, as in the ignition of carbonate of lime; or assumes the liquid state, as in the ignition of hydrate of lime; or solidifies, as in the ignition of a mixture containing chloride of ammonium—is a matter of perfect indifference as regards the name given to the operation.

The process of ignition is mostly employed, as has just been said, to effect the elimination of a volatile body. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus the sesquioxide of chro-

mium is converted by ignition into its insoluble modification, &c. In analytical investigations substances under examination are often ignited also, that the operator may from their deportment at a red heat draw a conclusion as to their nature in general; their fixity, their fusibility, the presence or absence of organic matter, &c.

Crucibles are the vessels made use of in ignition. In operations on a large scale Hessian or black-lead crucibles are used, heated by charcoal or coke; in analytical experiments small-sized crucibles or dishes are selected, of porcelain, platinum, silver, or iron, or glass tubes sealed at one end, according to the nature of the substances to be ignited; these crucibles, dishes, or tubes are heated over a *Berzelius* spirit-lamp or a properly-constructed gas-lamp.

§ 10.

9. Sublimation.

The term *sublimation* designates the process which serves to expand solid bodies into vapor by the application of heat, and subsequently to recondense the vapor to the solid state by refrigeration;—the substance volatilized and recondensed is called a *sublimate*. Sublimation is consequently a *distillation of solid bodies*. We have recourse to this process mostly to effect the separation of substances possessed of different degrees of volatility. Its application is of the highest importance in analysis for the detection of certain substances, *e. g.* of arsenic. The vessels used in sublimation are of various shapes, according to the different degrees of volatility of the substances operated upon. In sublimations for analytical purposes we generally employ sealed glass tubes.

§ 11.

10. Fusion and Fluxing.

We designate by the term " fusion" the conversion of a solid substance into the fluid form by the application of heat; fusion is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term " fluxing" is applied to this process in cases where substances insoluble or difficult of solution in water and acids are by fusion in conjunction with some other body modified or decomposed in such a manner, that they or the new-formed compounds will subsequently dissolve in water or acids. Fusion and fluxing are conducted either in porcelain, silver, or platinum crucibles, according to the nature of the compound. The crucible is supported on a triangle of moderately stout platinum wire, resting on, or attached to, the ring of the spirit or gas-lamp. Triangles of thick iron wire, especially when laid upon the still stouter brass ring of the lamp, carry off too much heat to allow of the production of very high temperatures. Small quantities of matter are also often fused in glass tubes sealed at one end.

Resort to fluxing is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates. The flux most commonly used is carbonate of soda or carbonate of potassa, or, better still, a mixture of both in equal atomic proportions (see § 75). In certain cases, hydrate of baryta is used instead of the alkaline carbonates (see § 76). But in either case the operation is conducted in platinum crucibles.

I have to add here a few precautionary rules for the prevention of

damage to the platinum vessels used in these operations. No substance evolving chlorine ought to be treated in platinum vessels; no nitrate of potassa, caustic potassa, metals, sulphides of the metals, or cyanides of the alkalies, should be fused in such vessels; nor ought readily deoxidizable metallic oxides, organic metallic salts, or phosphates to be ignited in them in the presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them directly to an intense charcoal fire, since the action of the ash, under such circumstances, gives readily rise to the formation of silicide of platinum, which renders the vessel brittle. It is always advisable to support the platinum crucible in which a process of ignition or fusion is to be conducted, on a triangle of platinum wire. Soiled platinum crucibles are cleaned by fusing in them bisulphate of potassa, and boiling afterwards with water.

We have still to speak here of another operation which bears some affinity to fusion.

§ 12.

11. Deflagration.

We understand by the term "*deflagration*," in a more general sense, every process of decomposition attended with noise or detonation—(the *cause* of the decomposition is a matter of perfect indifference as regards the application of the term in this sense).

We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another substance mixed with it (usually a nitrate or a chlorate), and connect with it the idea of a sudden and violent combustion attended with vivid incandescence and noise or detonation. Deflagration is resorted to either to produce the desired oxide—thus tersulphide of arsenic is deflagrated with nitrate of potassa to obtain arsenate of potassa;—or it is applied as a means to prove the presence or absence of a certain substance—thus salts are tested for nitric or chloric acid, by fusing them in conjunction with cyanide of potassium, and observing whether this process will cause deflagration or not, &c.

To attain the former object, the perfectly dry mixture of the substance under examination and of the deflagrating agent is projected in small portions into a red-hot crucible. Experiments of the latter description are invariably made with very minute quantities; the process is, in such cases, best conducted on a piece of thin platinum foil, or in a small spoon.

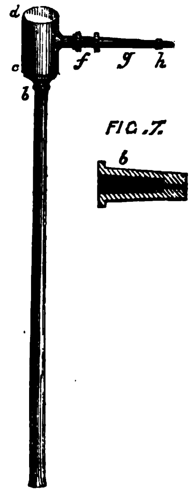
§ 13.

12. The Use of the Blowpipe.

This operation belongs exclusively to the province of analytical chemistry, and is of paramount importance in many analytical processes. We have to examine here, 1, the apparatus; 2, the mode of its application; and, 3, the results of the operation.

The blowpipe (Fig. 6) is a small instrument, usually made of brass or German silver. It was originally used by metallurgists for the purpose of soldering, whence it derived the name of "soldering-pipe" (*Löthrohr*) by which the Germans designate it. It consists of three distinct parts;

viz. 1st, a tube (a b), fitted, for greater convenience, with a horn or ivory mouthpiece, through which air is blown from the mouth ; 2nd, a small cylindrical vessel (c d), into which a b is screwed air-tight, and which serves as an air-chamber, and to retain the moisture of the air blown into the tube ; and, 3rd, a smaller tube (f g), also fitted into the vessel (c d). This small tube, which forms a right angle with the larger one, is fitted at its aperture either simply with a finely perforated platinum plate, or more conveniently with a finely perforated platinum cap (h) screwed in air-tight. The construction of the cap is shown in Fig. 7. It is, indeed, a little dearer than a simple plate, but it is also much more durable. Whenever the opening of the cap happens to be stopped up, the obstruction may be removed by heating the cap to redness before the blowpipe.



Figs. 6, 7.

The proper length of the blowpipe depends upon the distance to which the operator can see with distinctness ; it is usually from twenty to twenty-five centimètres. The form of the mouthpieces varies. Some chemists like them of a shape to be encircled by the lips ; others prefer the form of a trumpet mouthpiece, which is only pressed against the lips. The latter require less exertion on the part of the operator, and are accordingly generally chosen by those who have a great deal of blowpipe work.

The blowpipe serves to conduct a continuous fine current of air into a gas-flame, or into the flame of a candle or lamp. The flame of a candle (and equally so that of gas or of an oil lamp), burning under ordinary circumstances, is seen to consist of three distinct parts, as shown in Fig. 8, viz., 1st, a dark nucleus in the centre (a) ; 2nd, a luminous cone surrounding this nucleus (e f g) ; and, 3rd, a feebly luminous mantle encircling the whole flame (b c d). The dark nucleus is formed by the gases which the heat evolves from the wax or fat, and which cannot burn here for want of oxygen. In the luminous cone these gases come in contact with a certain amount of air insufficient for their complete combustion. In this part, therefore, it is principally the hydrogen of the carbides of hydrogen evolved which burns, whilst the carbon separates in a state of intense ignition, which imparts to the flame the luminous appearance observed in this part. In the outer coat, the access of air is no longer limited, and all the gases not yet burned are consumed here. This part of the flame is the hottest ; oxidizable bodies oxidize therefore with the greatest possible rapidity when placed in it, since all the conditions of oxidation are here united, viz. high temperature, and an unlimited supply of oxygen. This outer part of the flame is therefore called the *oxidizing flame*.


Fig. 8.

On the other hand, oxides having a tendency to yield up their oxygen, suffer *reduction* when placed within the *luminous* part of the flame, the

oxygen being withdrawn from them by the carbon and the still unconsumed carbide of hydrogen present in this sphere. The luminous part of the flame is therefore called the *reducing flame.*

Now the effect of blowing a fine current of air across a flame, is first to alter the shape of the latter, which, from tending upward, is now driven sideways in the direction of the blast, and at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part. As the latter circumstance causes an extraordinary increase of the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the exceedingly energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the current, will always depend upon the precise object in view, viz., whether the operator wants a *reducing* or an *oxidizing* flame. The easiest way of producing most efficient flames of both kinds is by means of coal-gas delivered from a tube, terminating in a flat top with a somewhat slantingly downward-turned slit 1 centimètre long and 1½ to 2 millimètres wide; as with the use of gas the operator is enabled to control and regulate not only the blowpipe flame, but the gas stream also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting that instrument upon some moveable metallic support, such as, for instance, the ring of *Bunsen's* gas lamp for supporting dishes, &c.

Fig. 9 shows the flame for reducing, Fig. 10 the flame for oxidizing. The luminous parts are shaded.

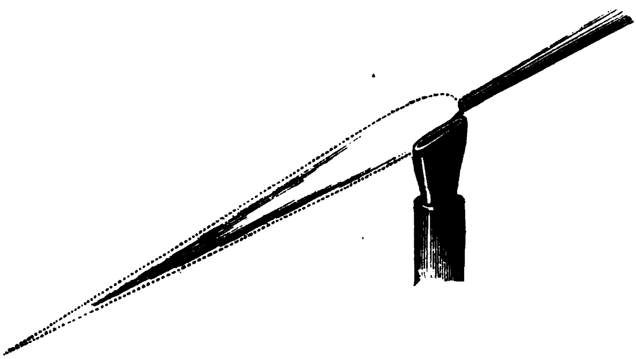


Fig. 9.

The *reducing* flame is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone. To produce the oxidizing flame, the gas is lowered, the jet of the blowpipe pushed a little further into the flame, and the strength of the current somewhat increased. This serves to effect an intimate mixture of the air and gas, and an inner pointed, bluish cone, slightly luminous towards the apex is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible bodies are exposed to this part to effect

their fusion; but bodies to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion. An oil-lamp with broad wick of proper thickness may be used instead of coal-gas; a thick wax candle also will do. For an oxidizing flame, a small spirit-lamp will in most cases answer the purpose.

Fig. 10.

The *current* is produced with the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by practising for some time to breathe calmly with puffed-up cheeks, and with the blowpipe between the lips; with a little patience the student will soon be able to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood, charcoal, or platinum wire or foil.

Charcoal supports are used principally in the reduction of metallic oxides, &c., or in trying the fusibility of bodies. The substances to be operated upon are put into small conical cavities scooped out with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame, evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame, the metallic fumes are re-oxidized, and the oxide formed is deposited around the portion of matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colors leading to the detection of the metals. Thoroughly-burnt pieces of charcoal only should be selected for supports in blowpipe experiments, as imperfectly-burnt pieces are apt to spirt and throw off the matter placed on them. The charcoal of the wood of the pine, linden, or willow is greatly preferable for supports to that of harder and denser woods. Smooth pieces ought to be selected for supports, as knotty pieces are apt to spirt when heated, and throw off the matter placed on them. The most convenient way is to saw the charcoal of well-seasoned and straight-split pinewood into parallelopipedic pieces, and to blow or brush off the dust; they may then be handled without fear of soiling the hands. Those sides alone are used on which the annual rings are visible as circles or segments, as on the other sides the fused matters are apt to spread over the surface of the charcoal (*Berzelius*).

The properties which make charcoal so valuable as a material for supports in blowpipe experiments are — 1st, its infusibility; 2nd, its low conducting power for heat, which admits of substances being heated more strongly upon a charcoal than upon any other support; 3rd, its porosity, which makes it imbibe readily fusible substances, such as

borax, carbonate of soda, &c., whilst infusible bodies remain on the surface; 4th, its power of reducing oxides, which greatly contributes to effecting the reduction of oxides in the inner blowpipe flame.

We use *platinum wire*, and occasionally also *platinum foil*, in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them, and to watch the phenomena attending the solution, and mark the color of the bead.

The wire, which should be about the thickness of lute-strings, is cut into lengths of 8 centimètres, and each length twisted at both ends into a small loop (Fig. 11).

Fig. 11.

When required for use, the loop is moistened with a drop of water, then dipped into the flux, and the portion adhering exposed to the flame of a gas- or spirit-lamp. The bead produced, which continues to adhere to the loop, is let cool, then moistened again, a small portion of the substance to be examined added to it, and the loop finally exposed, according to circumstances, to the inner or to the outer blowpipe flame.

What renders the application of the blowpipe particularly useful in chemical experiments is the great expedition with which the intended results are attained. These results are of a twofold kind, viz., either they afford us simply an insight into the general properties of the examined body, and enable us accordingly only to determine the *class* to which it belongs, *i. e.*, whether it is fixed, volatile, fusible, &c.; or the phenomena which we observe enable us at once to recognise the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the different substances with reagents.

APPENDIX TO SECTION I.

§ 14.

Apparatus and Utensils.

As many students of chemical analysis might find some difficulty in the selection of the proper apparatus, &c., I append here a list of the articles which are required for the performance of simple experiments and investigations, together with instructions to guide the student in the purchase or making of them.

1. A Berzelius Spirit-Lamp, with suitable stand. The part enclosing the wick and the vessel containing the spirit of wine must be in separate pieces, connected together by means of a narrow tube; otherwise most inconvenient explosions are apt to occur on lighting the lamp. The chimney must not be too narrow. The stopper on the mouth through which the spirit of wine is poured in must not fit airtight. The stand must be fitted with proper brackets, and also with a moveable brass ring to support dishes and flasks in processes of ebullition, and a ring of moderately stout iron wire to support

the triangle for holding the crucibles in the processes of ignition and fusion.

Of the various forms of lamps to be had, the one shown in Fig. 12 is the most suitable and elegant. Fig. 13 shows a triangle of platinum

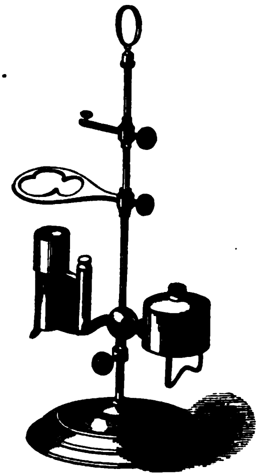


Fig. 12.

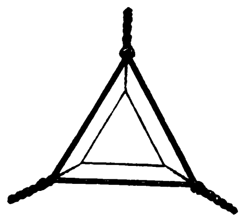
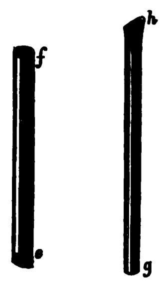


Fig. 13.

Fig. 14.

wire fixed within an iron wire triangle; this is the most suitable construction for supporting the crucible in processes of ignition. Glass vessels, more particularly beakers, which it is intended to heat over the lamp, are most conveniently rested on a circular piece of gauze made of fine iron wire such as is used in the making of sieves of medium fineness.



2. A Glass Spirit Lamp, with ground glass cap and brass wick-holder. (Fig. 14.)

In towns lighted by gas, spirit lamps are now almost entirely superseded by *gas lamps*. Of the many gas lamps proposed, *Bunsen's*, as shown in its simplest form in Fig. 15, is the most convenient. *a b* is a foot of cast-iron measuring 7 centimètres in diameter. In the centre of this is fixed a square brass box, *c d*, which slightly slants towards the top; the sides of this box are 25 millimètres high and 16 millimètres wide; it has a cylindric cavity 12 millimètres deep and 10 millimètres in diameter. Each side of the box has, 4 millimètres from the upper rim, a circular aperture of 8 millimètres diameter, leading to the inner cavity. One of the sides has fitted into it, about 1 millimètre

Fig. 15.

below the circular aperture, a tube to which is attached some vulcanized india-rubber, which serves to convey the gas to the apparatus. This tube is turned as shown in Fig. 15; it has a bore of 4 millimètres diameter. The gas conveyed into it through the india-rubber re-issues from a tube placed in the centre of the cavity of the box. This tube, which is 4 millimètres thick at the top, thicker at the lower end, projects 3 millimètres above the rim of the box; the gas issues from a narrow opening which appears formed of 3 radii of a circle, two of them forming an angle of 120° with one another. The length of each radius is 1 millimètre, the opening $\frac{1}{3}$ millimètre wide; *e f* is a brass tube 75 millimètres long, open at both ends, and having an inner diameter of 9 millimètres; the screw at the lower end of this tube fits into a nut in the upper part of the cavity of the box. With this tube screwed in, the lamp is completed. On opening the stop-cock, the gas rushes from the opening into the tube *e f*, when it mixes with the air coming in through the circular apertures (*c*). When this mixture is kindled at *f*, it burns with a straight, bluish flame, entirely free from soot, which may be regulated at will by opening the stop-cock more or less; a partial opening of the cock suffices to give a flame fully answering the purpose of the common simple spirit lamp; whilst, with the full stream of gas turned on, the flame, which will now rise up to 2 decimètres in height, burning with a roaring noise, affords a most excellent substitute for the Berzelius lamp. Flasks, &c., which it is intended to heat over the gas lamp, are most conveniently supported on wire gauze. If it is wished to use the gas lamp for blowpipe operations, the tube *g h* must be inserted into *e f*; this tube terminates in a flattened top slanting at an angle of 68°, to the axis, and having an opening in it 1 centimètre long and $1\frac{1}{2}$ to 2 millimètres wide; its insertion into *e f* serves to close up the air-apertures in the box, and pure gas, burning with a luminous flame, issues accordingly now from the top of the tube. Fig. 16 shows the apparatus complete, fixed in the forked iron stand; this arrangement permits the lamp being moved backward and forward between the prongs of the fork, and up and down the pillar of the stand. The moveable ring on the same pillar serves to support the object to be operated upon. The 6 radii round the tube of the lamp serve to support a porcelain plate used in quantitative analyses.

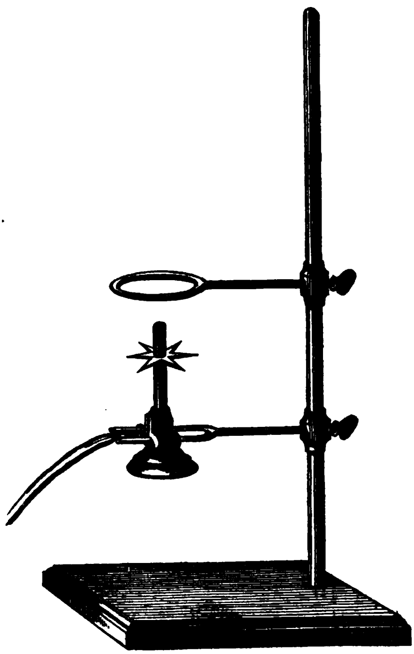


Fig. 16.

3. A BLOWPIPE (see § 13).

4. A PLATINUM CRUCIBLE which will contain about a quarter of an ounce of water, with a cover of the form of a shallow dish; it must not be too deep in proportion to its breadth.

5. PLATINUM FOIL, as smooth and clean as possible, and not very thin: length about 40 millimètres; width about 25 millimètres.

6. PLATINUM WIRE (see § 13); three or four wires are amply sufficient. They are kept most conveniently in a glass filled with water, most of the beads being dissolved by that fluid when left in contact with it for some time; the wires may thus be always kept clean.

7. A STAND WITH TWELVE TEST TUBES—16 to 18 centimètres is about the proper length of the tubes, from 1 to 2 centimètres the proper width. The pegs on the upper shelf serve for the clean tubes, which may thus be always kept dry and ready for use. The tubes must be made of thin white glass, and so well annealed that they do not crack even though boiling water be poured into them. The rim must be quite round, and slightly turned over; it ought not to have a lip, as this is useless, simply preventing the tube being closely stopped with the finger, and also shaking the contents.

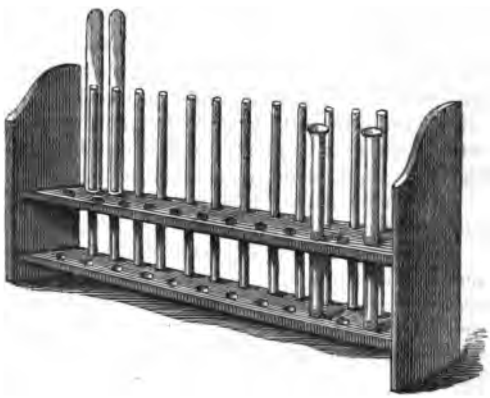


Fig. 17.

8. SEVERAL BEAKER GLASSES AND SMALL RETORTS of thin, well annealed glass.

9. SEVERAL PORCELAIN EVAPORATING DISHES, AND A VARIETY OF SMALL PORCELAIN CRUCIBLES. Those of the royal manufacture of Berlin are unexceptionable, both in shape and durability.

10. SEVERAL GLASS FUNNELS of various sizes. They must be inclined at an angle of 60°, and merge into the neck at a definite angle.

11. A WASHING BOTTLE of a capacity of from 300 to 400 cubic centimètres (see § 6).

12. SEVERAL GLASS RODS AND GLASS TUBES. The latter are bent, drawn out, &c., over a Berzelius spirit lamp; the former are rounded at the ends before the blowpipe.

13. A selection of WATCH-GLASSES.

14. A small AGATE MORTAR.

15. A pair of small STEEL or BRASS PINCERS, about four or five inches long.

16. A WOODEN FILTERING STAND (see § 5).

17. A TRIPOD of thin iron, to support the dishes, &c., which it is intended to heat over the small spirit or gas lamp.

SECTION II.

REAGENTS.

§ 15.

A VARIETY of phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color, in others precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, &c. Now, if these phenomena are very striking, and attendant only upon the action of two definite bodies upon one another, it is obvious that the presence of one of these bodies may be detected by means of the other: if we know, for instance, that a white precipitate of certain definite properties is formed upon mixing baryta with sulphuric acid, it is clear that, if upon adding baryta to any liquid, we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena are called *reagents.*

According to the different objects attained by their application we make a distinction between *general* and *special* reagents. By *general* reagents we understand those which serve to determine the *class* or *group* to which a substance belongs; and by *special* reagents those which serve to detect and determine bodies individually. That the line between the two divisions cannot be drawn with any degree of precision, and that one and the same substance is often made to serve both as a general and a special reagent, cannot well be held a valid objection to this classification, which, in fact, is simply intended to induce a habit of employing reagents always for a settled purpose—viz., either simply to find out the *group* to which the substance under examination belongs, or to determine the latter *individually.*

Now whilst the usefulness of *general* reagents depends principally upon their efficiency in strictly characterizing groups of bodies, and often effecting a complete separation of the bodies belonging to one group from those belonging to another, that of *special* reagents depends upon their being *characteristic*, and upon their being *sensitive.* We call a reagent *characteristic*, if the alteration produced by it, in the event of the body tested for being present, is so distinctly marked as to admit of no mistake. Thus, iron is a characteristic reagent for copper, protochloride of tin for mercury, because the phenomena produced by these reagents—viz., the separation of metallic copper and of globules of mercury, admit of no mistake. We call a reagent *sensitive* or *delicate*, if its action is distinctly perceptible, even though a very minute quantity only of the substance tested for be present; such is, for instance, the action of starch upon iodine.

Very many reagents are *both* characteristic and delicate; thus, for instance, terchloride of gold for protoxide of tin; ferrocyanide of potassium for sesquioxide of iron and oxide of copper, &c.

I need hardly mention that, as a general rule, reagents must be chemically pure—*i.e.*, they must consist purely and simply of their essential

constituents, and must contain no admixture of foreign substances. We must therefore make it an invariable rule to *test the purity of our reagents before we use them,* no matter whether they be articles of our own production or purchased. Although the *necessity* of this is fully admitted on all hands, yet we find that in *practice* it is too often neglected; thus it is by no means uncommon to see alumina entered among the substances detected in an analysis, simply because the solution of potassa used as one of the reagents happened to contain that earth; or iron, because the chloride of ammonium used was not free from that metal. The directions given in this section for testing the purity of the several reagents, refer, of course, only to the presence of foreign matter resulting from the mode of their preparation, and not to mere accidental admixture.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "*addition in excess*," "*supersaturation*," &c., often induce novices to suppose that they cannot add *too* much of the reagent, and thus some will *fill* a test tube with acid, simply to *supersaturate* a few drops of an alkaline fluid, whereas *every drop* of acid added, after the neutralization point has once been reached, is to be looked upon as an *excess* of acid. On the other hand, the addition of an insufficient amount is to be equally avoided, since a reagent, when added in insufficient quantity, often produces phenomena quite different from those which will appear if the same reagent be added in excess: *e.g.*, a solution of chloride of mercury yields a *white* precipitate, if tested with a *small* quantity of hydrosulphuric acid; but if treated with the same reagent *in excess*, the precipitate is *black*. Experience has, however, proved that the most common mistake beginners make, is to add the reagents too copiously. The reason why this over-addition must impair the accuracy of the results, is obvious; we need simply bear in mind that the changes effected by reagents are perceptible within certain limits only, and that therefore they may be the more readily overlooked the nearer we approach these limits by diluting the fluid.

No special and definite rules can be given for avoiding this source of error; a general rule may, however, be laid down, which will be found to answer the purpose, if not in all, at least in the great majority of cases. It is simply this: *let the student always reflect, before the addition of a reagent, for what purpose he applies it, and what are the phenomena he intends to produce.*

We divide reagents into two classes, according to whether the state of fluidity which is indispensable for the manifestation of the action of reagents upon the various bodies, is brought about by the application of heat, or by means of liquid solvents; we have consequently, 1, *Reagents in the humid way*; and 2, *Reagents in the dry way.* For greater clearness we subdivide these two principal classes as follows:—

A. REAGENTS IN THE HUMID WAY.

I. Simple Solvents.

II. Acids (and Halogens).

a. Oxygen acids.
b. Hydrogen acids and halogens.
c. Sulphur acids.

III. BASES (and METALS).

a. Oxygen bases.
b. Sulphur bases.

IV. SALTS.

a. Of the alkalies.
b. Of the alkaline earths.
c. Of the oxides of the heavy metals.

V. COLORING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOWPIPE REAGENTS.

A. REAGENTS IN THE HUMID WAY.

I. SIMPLE SOLVENTS.

Simple solvents are fluids which do not enter into chemical combination with the bodies dissolved in them; they will accordingly dissolve any quantity of matter up to a certain limit, which is called the point of saturation, and is in a measure dependent upon the temperature of the solvent. The essential and characteristic properties of the dissolved substances (taste, reaction, color, &c.) are not destroyed by the solvent. (See § 2.)

§ 16.

1. WATER (H O).

Preparation.—Pure water is obtained by distilling spring water from a copper still, with head and condenser made of pure tin, or from a glass retort; which latter apparatus, however, is less suitable for the purpose. The distillation is carried to about three-fourths of the quantity operated upon. If it is desired to have the distilled water perfectly free from carbonic acid, and carbonate of ammonia, the portions passing over first must be thrown away. In the larger chemical, and in most pharmaceutical laboratories, the distilled water required is obtained from the steam apparatus which serves for drying, heating, boiling, &c. Rain water collected in the open air may in many cases be substituted for distilled water.

Tests.—Pure distilled water must be colorless, inodorous, and tasteless, and must leave no residue upon evaporation in a platinum vessel. Sulphide of ammonium must not alter it (copper, lead, iron); its transparency must not be in the least impaired by basic acetate of lead (carbonic acid, carbonate of ammonia), nor, even after long standing, by oxalate of ammonia (lime), chloride of barium (sulphates), or nitrate of silver (metallic chlorides).

Uses.—We use water* principally as a simple solvent for a great variety of substances; the most convenient way of using it is with the washing bottle (see § 6, Fig. 3), by which means a large or fine stream may be obtained. It serves also to effect the conversion of several neutral metallic salts (more particularly terchloride of antimony and the salts of bismuth) into soluble acid, and insoluble basic compounds.

* In analytical experiments we use only *distilled* water; whenever, therefore, the term "water" occurs in the present work, distilled water is meant.

§ 17.

2. Alcohol ($C_4 H_6 O_2 = Ae O, H O$).

Preparation.—Two sorts of alcohol are used in chemical analyses: viz., 1st, spirit of wine of 0·83 or 0·84 spec. gr. = 91 to 88 per cent. by volume (*spiritus vini rectificatissimus* of the shops); and 2nd, absolute alcohol. The latter may be prepared by distilling the former from fused chloride of calcium, or by adding to it perfectly dry potassa, or anhydrous sulphate of copper, shaking the mixture, decanting the fluid, and redistilling it.

Tests.—Pure alcohol must completely volatilize, and ought not to leave the least smell of fusel oil, when rubbed between the hands; nor should it redden litmus paper. When kindled, it must burn with a faint bluish, barely perceptible flame.

Uses.—Alcohol serves, (*a*) to effect the separation of bodies soluble in this fluid from others which do not dissolve in it, *e.g.*, of chloride of strontium from chloride of barium; (*b*) to precipitate from aqueous solutions many substances which are insoluble in dilute alcohol, *e.g.*, gypsum, malate of lime; (*c*) to produce various kinds of ether, *e.g.*, acetic ether, which is characterized by its peculiar and agreeable smell; (*d*) to reduce, mostly with the co-operation of an acid, certain peroxides and metallic acids, *e.g.*, binoxide of lead, chromic acid, &c.; (*e*) to detect certain substances which impart a characteristic tint to its flame, especially boracic acid, strontia, potassa, soda, and lithia.

§ 18.

3. Ether ($C_4 H_5 O = Ae O$).

Ether finds but very limited application in the analysis of inorganic bodies. It serves, indeed, almost exclusively to detect and isolate bromine, and for this purpose the officinal ether of commerce is sufficiently pure and strong.

II. ACIDS AND HALOGENS.

§ 19.

The acids—at least those of more strongly pronounced character—are soluble in water. The solutions taste acid, and redden litmus paper. Acids are divided into oxygen acids, sulphur acids, and hydrogen acids.

The *oxygen acids* produced generally by the combination of a non-metallic element with oxygen, combine with water in definite proportions to hydrated acids. It is with these hydrates that we have usually to do in analytical processes; they are commonly designated by the name of "free acids," as the accession of the water does not destroy the acid properties. In the action of hydrated acids upon oxides of metals, the oxide takes the place of the water of hydration, and an oxygen salt is formed ($H O, S O_3 + K O = K O, S O_3 + H O$). Where these salts are the product of the combination of an acid with a strong base, their reaction (supposing the combining acid also to be a strong acid) is neutral; the salts formed with weaker bases, for instance, with the oxide of a heavy metal, generally show acid reaction, but are nevertheless called neutral salts, if the oxygen of the base bear the same proportion to that of the acid in which it is found in the distinctly neutral

salts of the same acid, or, in other terms, if it corresponds with the saturation capacity of the acid. Sulphate of potassa ($K\,O, S\,O_3$) has a neutral reaction, whilst the reaction of sulphate of copper ($Cu\,O, S\,O_3$) is acid; yet the latter is nevertheless called neutral sulphate of copper, because the oxygen of the oxide of copper in it bears a proportion of 1 : 3 to that of the sulphuric acid, which is the same proportion as the oxygen of the potassa bears to that of the sulphuric acid in the confessedly neutral sulphate of potassa.

The *hydrogen acids* are formed by the combination of the salt radicals with hydrogen. Most of these possess the characteristic properties of acids in a high degree. They neutralize oxygen bases with formation of haloid salts and water, $H\,Cl$ and $Na\,O = Na\,Cl$ and $H\,O = 3\,H\,Cl$ and $Fe_2\,O_3 = Fe_2\,Cl_3$ and $3\,H\,O$. The haloid salts produced by the action of powerful hydrogen acids upon strong bases, have a neutral reaction; whilst the solution of these haloid salts show acid reactions, which have been produced by the action of powerful hydrogen acid upon weak bases (such as the oxides of the heavy metals).

The *sulphur acids* are more frequently the result of the combination of metallic than of non-metallic elements with sulphur; they combine with sulphur bases to sulphur salts, $H\,S + K\,S = K\,S, H\,S, - Sb\,S_5 + 3\,Na\,S = 3\,Na\,S, Sb\,S_5$. The sulphur acids being weak acids, the soluble sulphur salts have all of them alkaline reaction.

a. OXYGEN ACIDS.

§ 20.

1. Sulphuric Acid ($H\,O, S\,O_3$).

We use—

a. Concentrated sulphuric acid of commerce, generally known in Germany as *English sulphuric acid.*

b. Concentrated pure sulphuric acid.

To be prepared as follows: heat sulphuric acid of commerce in a porcelain dish to about 230° F., and add, whilst stirring, small portions of dry oxalic acid (*Löwe*), or of dry sulphate of ammonia (*Pelouze*), until a portion of the acid taken out and cooled no longer turns red when solution of sulphate of protoxide of iron is poured upon it—a sign that every trace of hyponitric acid and nitric acid is gone. Add now (in the open air) pure dry chloride of sodium (about ½ per cent.) in small portions, with frequent stirring, and heat until the hydrochloric acid is completely expelled. All the arsenic originally present in the sulphuric acid is carried off with the fumes of the hydrochloric acid (*Löwe, A. Buchner*). The acid so purified is fit for nearly all the purposes of chemical analysis; if it is wished, however, to free it also from non-volatile substances, it may be distilled from a luted non-tubulated retort resting on a reversed crucible cover, and heated directly over charcoal. The lowest part of the retort, where the sulphate of lead, &c., is deposited, being thus in some measure protected by the interposed cover from the direct action of the fire, gets less strongly heated than the sides, which prevents the inconvenient and dangerous bumping of the liquid in the retort (compare *Graham—Otto,* ii. 1, p. 275). The neck of the retort must reach so far into the receiver that the acid distilling over drops directly into the body. Refrigeration of the receiver by means of

water is unnecessary and even dangerous. To prevent the flask coming into direct contact with the hot neck of the retort, some asbestos in long fibres is wrapt round that part of the neck where such contact might be apprehended.

c. Dilute sulphuric acid. This is prepared by adding to 5 parts of water in a leaden, or porcelain dish, gradually, and whilst stirring, 1 part of concentrated sulphuric acid. The sulphate of lead which separates is allowed to subside, and the clear fluid finally decanted from the precipitate.

Tests.—Pure sulphuric acid must be colorless; when colorless solution of sulphate of protoxide of iron is poured upon it in a test tube, no red tint must mark the line of contact of the two fluids (nitric acid, hyponitric acid); when diluted with twenty parts of water, it must not impart a blue tint to a solution of iodide of potassium mixed with starch paste (hyponitric acid).

When mixed with pure zinc and water, it must yield hydrogen gas; which, on being passed through a red-hot tube, must not deposit the slightest trace of arsenic. It must leave no residue upon evaporation on platinum, and must remain perfectly clear upon dilution with four or five parts of spirit of wine (oxide of lead, sesquioxide of iron, lime). The presence of small quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test tube. If the point of contact is marked by turbidity (chloride of lead), lead is present. (*Löwenthal.*)

Uses.—Sulphuric acid has for most bases a greater affinity than almost any other acid; it is therefore used principally for the liberation and expulsion of other acids, especially of phosphoric, boracic, hydrochloric, nitric, and acetic acids. It serves also for the liberation of iodine from metallic iodides. In this latter process it oxidizes the metal at the expense of its own oxygen, and is accordingly reduced to the state of sulphurous acid. Several substances which cannot exist in an anhydrous state (*e. g.*, oxalic acid), are decomposed when brought into contact with concentrated sulphuric acid; this decomposition is owing to the great affinity which sulphuric acid possesses for water. The nature of the decomposed body may in such cases be inferred from the liberated products of the decomposition. Sulphuric acid is also frequently used for the evolution of certain gases, more particularly of hydrogen, and hydrosulphuric acid. It serves also as a *special* reagent for the detection and precipitation of baryta, strontia, and lead. What kind of sulphuric acid is to be used, whether the pure, or the purified acid, or the ordinary acid of commerce, whether concentrated or dilute, depends upon what the circumstances in each case may require. It will, however, be found that the necessary directions on this point are generally given in the present work.

§ 21.

2. Nitric Acid (HO, NO_5).

Preparation.—*a.* Heat crude nitric acid of commerce, as free as possible from chlorine, and of a specific gravity of at least 1·31*, in a glass retort, to boiling, with addition of some nitrate of potassa; let the distillate run into a receiver kept cool, and try from time to time whether it still continues to precipitate or trouble solution of nitrate of silver.

* A weaker acid will not suit.

As soon as this ceases to be the case, change the receiver, and distil until a trifling quantity only remains in the retort. Dilute the distillate with water until the specific gravity of the diluted acid is 1·2.

b. Dilute crude nitric acid of commerce of about 1·38 specific gravity, with two-fifths of its weight of water; add solution of nitrate of silver as long as a precipitate of chloride of silver continues to form; let the precipitate subside, decant the perfectly clear supernatant acid into a tubulated retort; add some nitrate of potassa, free from chlorine, and distil until only a small quantity remains, taking care to attend to the proper cooling of the fumes distilling over. Dilute the distillate, if necessary, with water until it has a specific gravity of 1·2.

Tests.—Pure nitric acid must be colorless, and leave no residue upon evaporation on platinum foil. Additions of solution of nitrate of silver, or of nitrate of baryta, must not cause the slightest turbidity in it. It is advisable to dilute the acid with water before adding the reagents, as otherwise nitrates will precipitate.

Uses.—Nitric acid serves as a chemical solvent for metals, oxides, sulphides, oxygen salts, &c. With metals, and sulphides of metals, the acid oxidizes the metal present first, at the expense of part of its own oxygen, and then dissolves the oxide, forming a nitrate. Most oxides are dissolved by nitric acid at once as nitrates; and so are also most of the insoluble salts with weaker acids, the latter being expelled in the process by the nitric acid. Nitric acid dissolves also salts with soluble, non-volatile acids, as *e. g.* phosphate of lime, with which it forms nitrate of lime and acid phosphate of lime. Nitric acid is used also as an oxidizing agent: for instance, to convert protoxide of iron into sesquioxide, protoxide of tin into binoxide, &c.

§ 22.

3. Acetic Acid ($HO, C_4H_3O_3 = HO, \bar{A}$).

A highly concentrated acetic acid is not required in qualitative analytical processes; the common acetic acid of commerce, which contains 25 per cent. of anhydrous acid, and has a specific gravity of 1·04, answers the purpose.

Tests.—Pure acetic acid must leave no residue upon evaporation, and —after saturation with carbonate of soda—emit no empyreumatic odor. Hydrosulphuric acid, solution of nitrate of silver, and solution of nitrate of baryta must not impair the transparency of the dilute acid, nor must sulphide of ammonium, after neutralization of the acid by oxide of ammonium. Solution of indigo must not lose its color, when heated with the acid.

If the acid is not pure, add some acetate of soda and redistil from a glass retort, not quite to dryness; if it contains sulphurous acid (in which case hydrosulphuric acid will produce a white turbidity in it), digest it first with some binoxide of lead or finely pulverized binoxide of manganese, and then distil with acetate of soda.

Uses.—Acetic acid possesses a greater solvent power for some substances than for others; it is used, therefore, to distinguish the former from the latter; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. Acetic acid is occasionally used also to acidulate fluids where it is wished to avoid the employment of mineral acids.

§ 23.

4. Tartaric Acid ($2\,HO, C_8\,H_4\,O_{10}, = 2\,HO, \bar{T}$).

The tartaric acid of commerce is sufficiently pure for the purposes of chemical analysis. It is kept best in powder, as its solution suffers decomposition after a time, a white film forming upon its surface. For use, it is dissolved in a little water with the aid of heat.

Uses.—The addition of tartaric acid to solutions of sesquioxide of iron, protoxide of manganese, and various other oxides of metals, prevents the usual precipitation of these metals by an alkali; this non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may therefore be employed to effect the separation of these metals from others, the precipitation of which it does not prevent. Tartaric acid forms a difficultly soluble salt with potassa, but not so with soda; it is, therefore, one of our best reagents to distinguish between the two alkalies.

b. HYDROGEN ACIDS AND HALOGENS.

§ 24.

1. Hydrochloric Acid ($H\,Cl$).

Preparation.—Pour a cooled mixture of seven parts of concentrated sulphuric acid and two parts of water over four parts of chloride of sodium in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath, until the evolution of gas ceases; conduct the evolved gas, by means of a double limbed tube, into a flask containing six parts of water, and take care to keep this vessel constantly cool. To prevent the gas from receding, the tube ought only to dip about one line into the water of the flask. When the operation is terminated, try the specific gravity of the acid produced, and dilute with water until it marks from 1·11 to 1·12. If you wish to ensure the absolute purity of the acid, and its perfect freedom from every trace of arsenic and chlorine, you must take care to free the sulphuric acid, intended to be used in the process, from arsenic and the oxygen compounds of nitrogen, according to the directions of § 20. A pure acid may also be prepared cheaply from the crude hydrochloric acid of commerce, by diluting the latter to a specific gravity of 1·12, and distilling the fluid, with addition of some chloride of sodium. If the crude acid contains chlorine, this should be removed first by the cautious addition of solution of sulphurous acid, before proceeding to the distillation; if, on the other hand, it contains sulphurous acid, this is removed in the same way by the cautious addition of some chlorine water.

Tests.—Hydrochloric acid intended for the purposes of chemical analysis must be perfectly colorless, and leave no residue upon evaporation. It must not impart a blue tint to a solution of iodide of potassium mixed with starch paste (chlorine), nor discolor a fluid made faintly blue with iodide of starch (sulphurous acid). Chloride of barium ought not to produce a precipitate in the highly diluted acid (sulphuric acid). Hydrosulphuric acid must leave it unaltered. Sulphocyanide of potassium must not impart the least red tint to the diluted acid.

Uses.—Hydrochloric acid serves as a solvent for a great many substances. It dissolves many metals and sulphides of metals, forming chlorides, with evolution of hydrogen or of hydrosulphuric acid. It dissolves lower and higher oxides in the form of chlorides, the solution being, in the case of the higher oxides, mostly attended with liberation of chlorine. Salts with insoluble or volatile acids are also converted by hydrochloric acid into chlorides, with separation of the original acid; thus carbonate of lime is converted into chloride of calcium, with liberation of carbonic acid. Hydrochloric acid dissolves salts with non-volatile and soluble acids, *apparently* without decomposing them (*e. g.*, phosphate of lime); but the fact is that, in cases of this kind, a metallic chloride and a soluble acid salt of the acid of the dissolved compound are formed; thus, for instance; in the case of phosphate of lime, chloride of calcium and acid phosphate of lime are formed. With salts of acids forming no soluble acid compound with the base present, hydrochloric acid forms metallic chlorides, the liberated acids remaining free in solution (borate of lime). Hydrochloric acid is also applied as a *special* reagent for the detection and separation of oxide of silver, suboxide of mercury, and lead (see below); and likewise for the detection of free ammonia, with which it produces in the air dense white fumes of chloride of ammonium.

§ 25.

2. Chlorine (Cl) and Chlorine Water.

Preparation.—Mix 18 parts of finely ground common salt with 15 parts of *finely pulverized* good binoxide of manganese; put the mixture in a flask, pour a *completely cooled* mixture of 45 parts of concentrated sulphuric acid and 21 parts of water upon it, and shake the flask: a uniform and continuous evolution of chlorine gas will soon begin, which, when slackening, may be easily increased again by the application of a *gentle* heat. This method of *Wiggers* is excellent, and can be highly recommended. Conduct the chlorine gas evolved, first through a flask containing a little water, then into a bottle filled with cold water, and continue the process until the fluid is saturated. The chlorine water must be kept in a cellar, and carefully protected from the action of light; since, if this precaution is neglected, it speedily suffers complete decomposition, being converted into dilute hydrochloric acid, with evolution of oxygen (resulting from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle, protected from the influence of light by a case of pasteboard. Chlorine water which has lost its strong peculiar odor is unfit for use.

Uses.—Chlorine has a greater affinity than iodine and bromine for metals and for hydrogen. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. Chlorine serves, moreover, to convert sulphurous acid into sulphuric acid, protoxide of iron into sesquioxide, &c.; and also to effect the destruction of organic substances, in presence of water, as it withdraws hydrogen from the latter, enabling thus the liberated oxygen to combine with the vegetable matters and to effect their decomposition. For this latter purpose it is most advisable to *evolve* the chlorine in the fluid which contains the organic substances; this is effected by adding hydrochloric acid to the fluid, heating the mixture to boiling, and then adding chlorate of potassa. This gives rise to the formation of chloride of potas-

sium, water, free chlorine, and bichlorate of chlorous acid, which acts in a similar manner to chlorine.

§ 26.

3. Nitro-Hydrochloric Acid. *Aqua regia.*

Preparation.—Mix one part of pure nitric acid with from three to four parts of pure hydrochloric acid.

Nitric acid and hydrochloric acid decompose each other, the decomposition resulting, in most cases, as *Guy-Lussac* has shown, in the formation of two compounds which are gaseous at the ordinary temperature, $N\,O_2\,Cl_2$ and $N\,O_2\,Cl$, and of free chlorine and water. If one equivalent of $N\,O_5$ is used to three equivalents of $Cl\,H$, it may be assumed that only chloro-hyponitric acid ($N\,O_2\,Cl_2$), chlorine and water, are formed ($N\,O_5 + 3\,H\,Cl = N\,O_2\,Cl_2 + Cl + 3\,H\,O$).

This decomposition occurs as soon as the fluid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the free chlorine, and also, but in a very subordinate degree, that of the acids named, makes aqua regia our most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine). Nitro-hydrochloric acid serves principally to effect the solution of gold and platinum, which metals are insoluble both in hydrochloric and in nitric acid; and also to decompose various metallic sulphides, *e. g.*, cinnabar, pyrites, &c.

§ 27.

4. Hydrofluosilicic Acid ($H\,F, S\,I\,F_2$).

Preparation.—Take quartz sand, wash off every particle of dust, and dry thoroughly. Mix one part of the dry sand intimately with one part of perfectly dry fluor spar in powder; pour six parts of concentrated sulphuric acid over the mixture in a strong glass flask or in a mineral water bottle dry inside, and mix carefully by shaking the vessel. As the mixture swells up, when getting warm, it must at first fill the vessel only to one-third. The mouth of the flask or bottle must be closed with a perforated cork, or a cap of india-rubber, into which one end of a somewhat wide glass tube, twice bent at a right angle, is fitted air-tight; the other limb reaching to the bottom of a tall flat-bottomed glass jar with just sufficient mercury to allow the end of the tube to dip into it to the extent of several lines; the mercury in the jar is covered with four parts of water. Promote the disengagement of fluosilicic gas, which commences even in the cold, by exposing the flask or bottle to a moderate heat in the sand-bath. Towards the end of the process a pretty strong heat should be applied. Every gas bubble ascending through the mercury produces in the water a precipitate of hydrated silicic acid. The rationale of this process is that, of every three equivalents of fluoride of silicon ($Si\,Fl_2$), one equivalent decomposes with two equivalents of water into silicic acid ($Si\,O_2$), which separates, and hydrofluoric acid, which combines with the two undecomposed equivalents of fluoride of silicon, forming hydrofluosilicic acid.

$$[3\,Si\,F_2 + 2\,H\,O = 2\,(H\,F, S\,I\,F_2) + Si\,O_2].$$

The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the exit tube must be placed

under mercury, since it would speedily be choked if this precaution were neglected. The same end may be attained also by attaching a funnel to the exit tube, by means of vulcanized india-rubber, and letting the funnel alone dip into the water. It sometimes happens in the course, and especially towards the end of the operation, that the gas forms complete channels of silica in the gelatinous liquid, through which it gains the surface without undergoing decomposition, if the liquid is not occasionally stirred. When the evolution of gas has completely ceased, throw the gelatinous paste upon a linen cloth, squeeze the fluid through, and filter it afterwards. Keep the filtrate for use.

Tests.—Hydrofluosilicic acid, mixed with two parts of water, must produce no precipitate in solutions of salts of strontia.

Uses.—Bases decompose with hydrofluosilicic acid, forming water and metallic silicofluorides. Many of these are insoluble, whilst others are soluble; the latter may therefore by means of this reagent be distinguished from the former. In the course of analysis, hydrofluosilicic acid is applied simply for the detection of baryta.

c. SULPHUR ACIDS.

§ 28.

5. Hydrosulphuric Acid (*Sulphuretted Hydrogen*) (H S).

Preparation.—Hydrosulphuric acid gas is evolved best from sulphide of iron, which is broken into small lumps, and then treated with dilute sulphuric acid. Fused sulphide of iron may be procured so cheaply in commerce that it is hardly worth while to take the trouble of preparing it expressly. However, if you wish to prepare it yourself, this may be done by heating iron turnings or nails, from 1 to 1½ inch long, in a Hessian crucible to a white heat, and then adding small lumps of roll-sulphur until the entire contents of the crucible are in fusion. As soon as this is the case, pour the fused mass out on sand, or into an old Hessian crucible. Or make a hole in the bottom of the crucible in which you fuse the mass, when the sulphide of iron will, as fast as it forms, run through the hole in the bottom of the crucible, and may thus be easily received in a coal-shovel placed in the ash-pit. Or, introduce an intimate mixture of thirty parts of iron filings and twenty-one parts of flowers of sulphur, gradually and in small portions at a time, into a red-hot crucible, awaiting always the incandescence of the portion last introduced, before proceeding to the addition of a fresh one. When you have thus put the whole mixture into the crucible, cover the latter closely, and expose it to a more intense heat, sufficient to make the sulphide of iron fuse more or less.

Fig. 18.

The evolution of the gas is effected in the apparatus illustrated by Fig. 18.

Pour water over the sulphide of iron in *a*, add concentrated sulphuric acid, and shake the mixture; the evolved gas is washed in *c*. When a sufficient quantity of gas is evolved, pour the fluid from off the still undecomposed sulphide of iron, wash the bottle repeatedly with water, fill it with that fluid, and keep it for next operation. If you neglect this, the apparatus will speedily become incrusted with crystals of sulphate of protoxide of iron, which is apt to interfere injuriously with subsequent processes of evolution of gas.

For larger laboratories, or for chemists, having to operate often and largely with hydrosulphuric acid, I can recommend the lead apparatus designed by myself, which I have now for several years employed with the most satisfactory results in my own laboratory* (see Figs. 19 and 20).

a b c d and *e f g h* (Fig. 20) are two cylindrical leaden vessels, soldered with pure lead. They are both of the same size (in my own apparatus 33

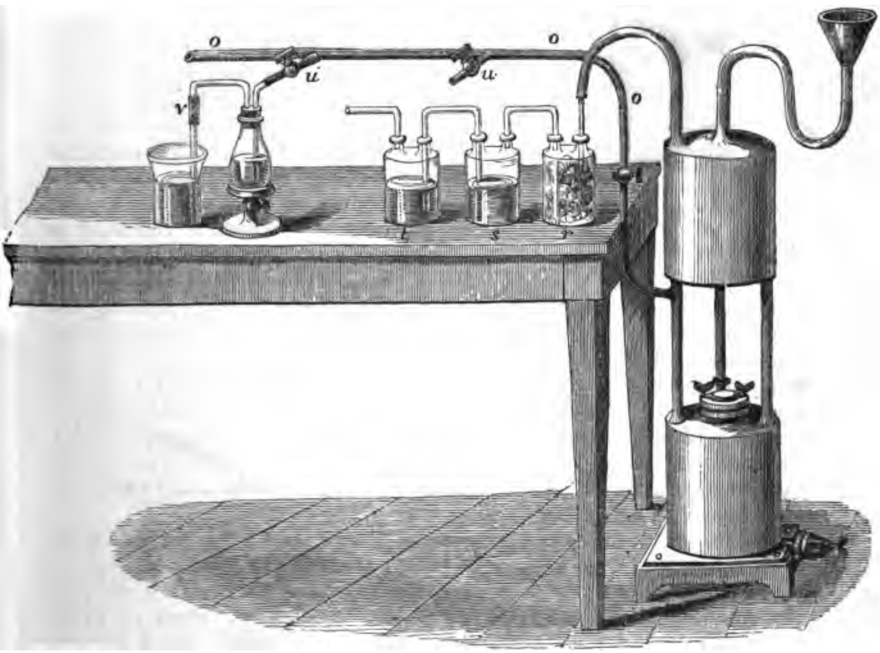


Fig. 19.

centimètres high, and 30 centimètres in diameter). *i* is a false bottom of lead, perforated like a sieve, placed from 4 to 5 centimètres above the actual bottom of the vessel, and resting on leaden feet, which support it on the sides as well as also more particularly in the middle. The numerous holes in the sieve-like bottom have a diameter of $1\frac{1}{2}$ milli-

* The apparatus is made by *Mr. Stumpf*, of Wiesbaden, mechanist, and fully answers all reasonable demands, both as regards workmanship and price.

mètres; *k* shows the opening through which the sulphide of iron is introduced into the vessel. In my apparatus this aperture has a diameter of 7 centimètres, and is closed by putting a greased leather ring on its broad smooth rim, and pressing down upon this by means of three winged screws, the broad rim of the smooth-turned cover. *l* shows the opening through which the solution of sulphate of protoxide of iron is drawn off; it will be seen by the drawing that the bottom of the vessel (*g h*) slants towards the part where this opening is placed. The aperture has a diameter of 3 centimètres; it is closed by means of a smooth-turned broad and thick leaden cap, fitting on the smooth-turned broad rim, and pressed down upon it with a winged screw. The semi-elliptical bar in which the female screw is set, is moveable, and hinged to the sides of *l* in a manner to admit of its being bent out of reach of the liquid on drawing off the latter. The construction of the filling tube, *m*, may be learned from the drawing, and equally so that of the tube *d h*, which is intended to convey the acid from the upper to the lower vessel, and *vice versâ*. It will be seen from the drawing that this tube reaches down into the slanting and deepened part of the bottom *g h*, without, however, actually touching the latter. The tube *c e* is closed at the top, and has, therefore, no communication with the upper vessel, being simply intended to let off the gas evolved in *e f g h*; to which end it is connected laterally by a branch tube, with the tube *o*; this latter tube is fitted with a stop-cock (*n*). The tube *q* is closed at both ends, and serves simply as an additional support for the upper vessel. The tubes in my apparatus have an inner diameter of 16 millimètres.

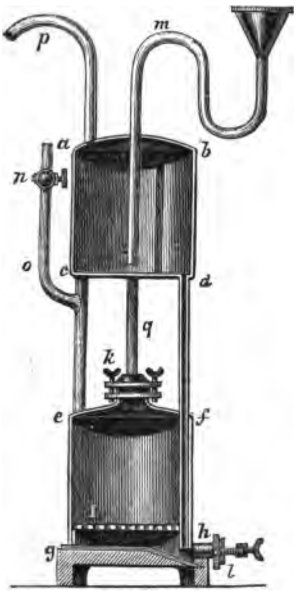


Fig. 20.

The process of filling is conducted as follows: put 3·3 kilogrammes* of fused sulphide of iron, broken in lumps, through the mouth *k*, upon the perforated bottom *i*; screw the covers properly down upon *k* and *l*, shut the cock *n*, and pour through the funnel of *m* first 7 litres of water, then 1 litre of concentrated sulphuric acid, and then again 7 litres of water. The air in *a b c d* escapes in this operation through *p*, even when the latter tube is already connected with the flasks *r*, *s*, *t*.

If the cock *n* is now opened, and one of the cocks *u*, the acid will flow through the tube *d l* into *e f g h*; and through *o* air will escape at first, followed by the hydrosulphuric acid evolved in *e f g h*. As is seen in the figure, the tube *o* rises only to a certain elevation, when it makes a bend, running on thence in a horizontal direction. As many cocks, *u u*, are added as is thought desirable; these cocks are common brass gas stop-

* The quantities here given are calculated for an apparatus of the dimensions stated.

cocks, close-fitting and well ground in. They are connected with a small washing bottle; a double-bent tube conveys the gas from the latter, with the co-operation of a straight tube connected with it by means of vulcanized india-rubber, into the fluid which it is intended to operate on; this arrangement greatly facilitates the cleansing of the straight tube dipping into the fluid. Upon now opening one of the cocks, *u*, the cock *n* being of course also open, you will at once obtain a current of gas of any strength desired, which will keep on for days in a continuous and steady stream. If all the cocks *u*, are shut, the gas evolved in *e f g h* forces the acid back to the upper vessel through the tube *h d*, and the evolution ceases.

The cessation of the evolution of gas is not instantaneous, however, as the sulphide of iron in *e f g h* remains still moistened with acid; moreover, small particles of the sulphides will always crumble off, and dropping through the sieve, come into contact with the rest of the acid covering the bottom, *g h*. Now the gas which still continues to be evolved in *e f g h*, being no longer able to escape through *o*, forces the fluid up *h d*, and passing through the acid in *a b c d*, makes its way out through *p*. To save this gas and keep it from poisoning the air, the flasks *r*, *s*, *t*, are connected with *p*. *r* contains cotton, and serves the purpose of a washing bottle;* *s* and *t* contain solution of ammonia; but the two flasks together should contain no more than either of them can conveniently hold; since, as the pressure of the gas increases or relaxes, the fluid is forced from *s* to *t*, or back from *t* to *s*. It will be readily understood that sulphide of ammonium is formed in these flasks.

The evolution of gas ceases completely when all the acid is consumed, but there remains still the one half of the sulphide of iron, as the quantity used is calculated for double the amount of acid. The solution of sulphate of protoxide of iron is therefore drawn off, and 1 litre of acid and 14 of water again poured in as directed. This apparatus is now made also of much less dimensions to adapt it for smaller laboratories. *Kipp* has devised a glass apparatus constructed upon the same principle. It is shown in Fig. 21. The drawing fully explains its construction and application.

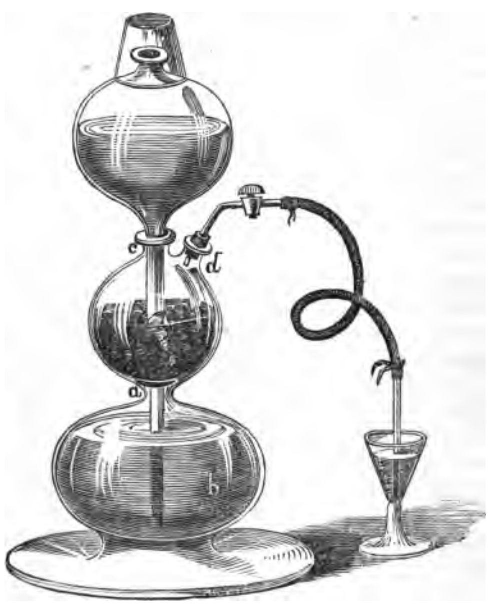


Fig. 21.

* A common washing bottle filled with water could not well be used, as the water would very speedily recede.

Sulphuretted hydrogen water (*solution of hydrosulphuric acid*) is prepared by conducting the gas into very cold water, which has been previously freed from air by boiling. The operation is continued until the water is completely saturated with the gas, which may be readily ascertained by closing the mouth of the flask with the thumb, and shaking it a little: if, upon this, a pressure is felt from within, tending to push the thumb off the aperture of the flask, the operation may be considered at an end; but if, on the contrary, the thumb feels sucked into the mouth of the flask, this is a sure sign that the water is still capable of absorbing more gas.

Sulphuretted hydrogen water must be kept in well-closed vessels, otherwise it will soon suffer complete decomposition, the hydrogen being oxidized to water, and a small portion of the sulphur to sulphuric acid, the rest of the sulphur separating. The best way of preserving it unaltered for a very long time is to pour the freshly-prepared solution immediately into small phials, and to place the latter, carefully corked, in an inverted position, into bottles filled with water.

Tests.—Pure sulphuretted hydrogen water must be perfectly clear, and strongly emit the peculiar odor of the gas; when treated with sesquichloride of iron, it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it. It must leave no residue upon evaporation on platinum.

Uses.—Hydrosulphuric acid has a strong tendency to undergo decomposition with metallic oxides, forming water and metallic sulphides; and the latter being mostly insoluble in water, are usually precipitated in the process. The conditions under which the precipitation of certain sulphides ensues differ materially; by altering or modifying these conditions, we may therefore divide the whole of the precipitable metals into groups, as will be found explained below. Hydrosulphuric acid is therefore an invaluable agent to effect the separation of metals into principal groups. Some of the precipitated sulphides exhibit a characteristic color indicative of the individual metals which they respectively contain. Hydrosulphuric acid serves thus more particularly for the *special* detection of tin, antimony, arsenic, cadmium, manganese, and zinc. For more ample information upon this point, I refer to the third section. The great facility with which hydrosulphuric acid is decomposed, renders this substance also a useful reducing agent for many compounds; thus it serves, for instance, to reduce salts of sesquioxide of iron to salts of protoxide, chromic acid to the state of sesquioxide of chromium, &c. In these processes of reduction, the sulphur separates in the form of a fine white powder. Whether the hydrosulphuric acid had better be applied in the gaseous form, or in aqueous solution, depends always upon the special circumstances of the case.

III. BASES AND METALS.

§ 29.

Bases are divided into oxygen bases and sulphur bases. The former result from the combination of metals or of compound radicals of similar character with oxygen, the latter from the combination of the same bodies with sulphur.

The *oxygen bases* are classified into alkalies, alkaline earths, earths proper, and oxides of the heavy metals. The alkalies are readily soluble

in water; the alkaline earths dissolve with greater difficulty in that menstruum; and magnesia, the last member of the class, is only very sparingly soluble in it. The earths proper, and the oxides of the heavy metals are insoluble in water, or nearly so. The solutions of the alkalies and alkaline earths are caustic when sufficiently concentrated; they have an alkaline taste, change the yellow color of turmeric paper to brown, and restore the blue tint of reddened litmus paper; they saturate acids completely, so that even the salts which they form with strong acids do not change vegetable colors, whilst those with weak acids generally have an alkaline reaction. The earths proper and the oxides of the heavy metals combine likewise with acids to form salts, but, as a rule, they do not entirely take away the acid reaction of the latter.

The *sulphur bases* resulting from the combination of the metals of the alkalies and alkaline earths with sulphur, are soluble in water. The solutions have a strong alkaline reaction. The other sulphur bases do not dissolve in water. All sulphur bases form with sulphur acids sulphur salts.

a. OXYGEN BASES.

a. Alkalies.

§ 30.

1. Potassa (K O) and Soda (Na O).

The preparation of perfectly pure potassa or soda is a difficult operation. It is advisable, therefore, to prepare, besides perfectly pure caustic alkali, also some which is not quite pure, and some which, being free from certain impurities, may in many cases be safely substituted for the pure substance.

a. Common solution of soda.

Preparation.—Put into a clean cast-iron pan provided with a lid, $5\frac{1}{2}$ parts of crystallized carbonate of soda of commerce and 20 parts of water, heat to boiling, and add, in small portions at a time, thick milk of lime prepared by pouring 4 parts of warm water upon $1\frac{1}{2}$ parts of quicklime, and letting the mixture stand in a covered vessel until the lime is reduced to a uniform pulpy mass. Keep the liquid in the pan boiling whilst adding the milk of lime, and for a quarter of an hour longer, then filter off a small portion, and try whether the filtrate still causes effervescence in hydrochloric acid. If this is the case, the boiling must be continued, and, if necessary, some more milk of lime added to the fluid. When the solution is perfectly free from carbonic acid, cover the pan, allow the fluid to cool a little, and then draw off the clear solution from the residuary sediment, by means of a syphon filled with water, and transfer it to a glass flask. Boil the residue a second and a third time with water, and draw off the fluid in the same way. Cover the flask close with a glass plate, and allow the lime suspended in the fluid to subside completely. Scour the iron pan clean, pour the clear solution back into it, and evaporate it to 11 or 12 parts. The solution so prepared contains from 9 to 10 per cent. of soda. It must be clear, colorless, and as free as possible from carbonic acid; sulphide of ammonium must not impart a black color to it. Traces of silicic acid, alumina, and phosphoric acid, are usually found in a solution of soda

prepared in this manner; on which account it is unfit for use in accurate experiments.

Solution of soda is kept best in bottles closed with ground glass caps. In default of capped bottles, common ones with ground stoppers may be used; but in that case, the neck must be wiped perfectly dry and clean inside, and a slip of writing paper rolled round the stopper; since, if these precautions are neglected, it will be found impossible, after a time, to remove the stopper, particularly if the bottle is only rarely opened.

b. Hydrate of potassa purified with alcohol.

Preparation.—Dissolve some sticks of caustic potassa of commerce in rectified spirit of wine in a stoppered bottle, by digestion and shaking; let the fluid stand, decant or filter if necessary, and evaporate the clear fluid in a covered silver dish over the spirit-lamp, until no more aqueous vapors escape; adding from time to time, during the evaporation, some water, to prevent blackening of the mass. Place the silver dish in cold water until it has sufficiently cooled; remove the cake of caustic potassa from the dish, break it into coarse lumps in a hot mortar, and keep in a well-closed glass bottle. When required for use, dissolve some of it in water.

The hydrate of potassa so prepared is sufficiently pure for most purposes; it contains, indeed, a minute trace of alumina, but is usually free from phosphoric acid, sulphuric acid, and silicic acid. The solution must remain clear upon addition of sulphide of ammonium; hydrochloric acid must only produce a barely perceptible effervescence in it. The solution, acidified with hydrochloric acid, must, upon evaporation to dryness, leave a residue which dissolves in water to a clear fluid; when boiled with molybdate of ammonia, it must exhibit no yellow colour; when treated with ammonia, it ought not to deposit slight flakes of alumina immediately; but only after standing several hours in a warm place.

c. Hydrate of potassa prepared with baryta.

Preparation.—Dissolve pure crystals of baryta (§ 32) by heating with water, and add to the solution pure sulphate of potassa, until a portion of the filtered fluid, acidified with hydrochloric acid and diluted, no longer gives a precipitate on addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of sulphate of potassa). Let the turbid fluid clear, decant, and evaporate in a silver dish as in *b.* The hydrate of potassa so prepared is perfectly pure, except that it contains a trifling admixture of sulphate of potassa, which is left behind upon dissolving the hydrate in a little water. This hydrate is but rarely required, its use being in fact exclusively confined to the detection of minute traces of alumina.

Uses.—The great affinity which the fixed alkalies possess for acids renders these substances powerful agents to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases which are insoluble in water. Many of the so precipitated oxides redissolve in an excess of the precipitant, as, for instance, alumina, sesquioxide of chromium, and oxide of lead; whilst others remain undissolved, *e. g.*, sesquioxide of iron, teroxide of bismuth, &c. The fixed alkalies serve therefore also as a means to separate the former from the latter. Potassa and soda dissolve also many salts (*e. g.*, chromate of lead), sulphur compounds, &c., and serve thus to separate and distinguish them from other substances. Many of the oxides precipitated by the action

of potassa or soda exhibit a peculiar color, or possess other characteristic properties that may serve to lead to the detection of the individual metal which they respectively contain; such are, for instance, the precipitate of protoxide of manganese, hydrate of protoxide of iron, suboxide of mercury, &c. The fixed alkalies expel ammonia from its salts, and enable us thus to detect that body by its smell, its reaction on vegetable colors, &c.

§ 31.

2. Ammonia—*Oxide of Ammonium*—($N H_4 O$).

Preparation.—The apparatus illustrated by Fig. 18 (§ 28) may also serve for the preparation of solution of ammonia, with this modification however, that no funnel tube being required in the process, the cork upon the flask *a* has only one perforation for the reception of the tube which serves to conduct the evolved ammonia into the washing bottle. Introduce into *a* 4 parts of chloride of ammonium in pieces about the size of a pea, and dry hydrate of lime prepared from 5 parts of lime; mix by shaking the flask, and add cautiously a sufficient quantity of water to make the powder into lumps. Put a small quantity of water only into the washing bottle (which should be rather capacious); but have 10 parts of water in the flask which is intended for the final reception of the washed gas. Set the flask *a* now in a sand bath, connect it with the rest of the apparatus, place the flask *d* in a vessel of cold water, and apply heat. The evolution of gas speedily commences. Continue to heat until no more bubbles appear. Open the cork of the flask *a*, to prevent the receding of the fluid. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver *d* is perfectly pure; dilute it with water until the specific gravity is about $0{\cdot}96 = 10$ per cent. of ammonia. Keep the fluid in bottles closed with ground stoppers. This is the best way of preparing solution of ammonia in small quantities. That prepared on a large scale in cast-iron vessels is of course cheaper.

Tests.—Solution of ammonia must be colorless, and ought not to leave the least residue when evaporated on a watch-glass, nor should it cause the slightest turbidity in lime water (carbonic acid). When supersaturated with nitric acid, neither solution of nitrate of baryta, nor of nitrate of silver, must render it turbid, nor must sulphuretted hydrogen impart to it the slightest color.

Uses.—Solution of ammonia, although formed by conducting ammoniacal gas ($N H_3$) into water, and letting that gas escape upon exposure to the air, and much quicker when heated, is conveniently regarded as a solution of oxide of ammonium ($N H_4 O$) in water, the equivalent of water ($H O$) existing with $N H_3$ being assumed to form with the latter $N H_4 O$. Solution of ammonia is accordingly regarded as corresponding to the solution of potassa and soda, which greatly serves to facilitate the explanation of many chemical transformations into which the ammoniacal compounds enter, the oxygen salts resulting from the neutralization of oxygen acids by solution of ammonia being also assumed to contain oxide of ammonium $N H_4 O$, instead of $N H_3$. In the present edition, therefore, ammonia signifies oxide of ammonium ($N H_4 O$), and corresponds to the oxides of potassium and sodium, or potassa and soda. Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the

precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in an excess of ammonia, as, for instance, the oxides of zinc, cadmium, silver, copper, &c., whilst others are insoluble in free ammonia. This reagent may serve, therefore, to separate and distinguish the former from the latter. Some of these precipitates, as well as their solutions in ammonia, exhibit peculiar colors, which may at once lead to the detection of the individual metal which they respectively contain.

Many of the oxides which are precipitated by ammonia from neutral solutions, are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the formation of a salt of ammonia. Compare § 51, choride of ammonium.

β. ALKALINE EARTHS.

§ 32.

1. Baryta (Ba O).

Preparation.—a. From sulphate of baryta. Mix together 6 parts of finely pulverized sulphate of baryta, 1 part of powdered charcoal, and $1\frac{1}{2}$ part of flour; or 8 parts of sulphate of baryta, 2 parts of charcoal, and 1 part of common resin. Put the mixture in a crucible, and expose it in a wind furnace to a long-continued red heat; or put the mixture in an earthen pot, lute the lid on with clay, and expose the pot to the heat of a brick-kiln. Boil the crude sulphide of barium obtained by this process for some time with water, and, when the crystallization point is attained, filter off hot: let the filtrate cool in a well-covered vessel. Pour off the mother liquor, which, together with the residue left from the boiling of the sulphide of barium, may be used for the preparation of chloride of barium; boil the crystals with just sufficient water to dissolve them; keep boiling (taking care to replace the evaporated water); add finely triturated and sifted copper scales in small portions at a time, until a filtered sample of the fluid gives a pure white precipitate when mixed with a little acetate of lead. Filter boiling. As solution of baryta eagerly absorbs carbonic acid from the air, great care must be taken to exclude the air in the processes of filtration and crystallization. To effect this it is necessary to place the beaker intended to receive the filtrate on a flat dish or flat iron pot containing a little milk of lime, invert a bell-glass over it with an opening in the top, insert the funnel through this, filter, then remove the funnel, close the opening in the top of the bell-glass with an india-rubber cap, and let the fluid thus protected from access of air stand for several days in a cool place. After this decant the fluid (baryta water), let the crystals (Ba O, H O + 8 aq.) drain in a well-covered funnel, dry them quickly between sheets of blotting-paper, and keep them in well-stoppered bottles. For use dissolve 1 part in 20 parts of water, and filter. The baryta water so obtained is preferable to that decanted from the crystals.

b. From nitrate of baryta. Project a mixture of 8 parts of finely pulverized nitrate of baryta and 3 parts of clean iron filings, a spoonful at a time, but not in too quick succession, into a ret-hot Hessian, or, better still, into a red-hot iron crucible. When the mass has left off

frothing, and become pasty and in the end friable, take it out with an iron spatula, let it cool, and when cool powder it. Boil the crucible now for half an hour with 64 parts of water in an iron pot, take the crucible out, put the powdered mass into the boiling fluid, add 16 parts more of water, boil another half hour, filter, and proceed with the filtrate as in *a* (*Wittstein*).

c. From Witherite. Mix intimately 100 parts of finely pulverized Witherite, 10 parts of powdered charcoal, and 5 parts of resin; or 100 parts of Witherite and 15 parts of finely powdered caking coal. Put the mixture in a pot or crucible, lute on the lid with clay, and expose to the heat of a brick-kiln. Triturate the mass, and boil the powder with water; filter, and proceed with the filtrate as in *a*. The undissolved residue, which consists of undecomposed Witherite and coal, may be used in the preparation of chloride of barium. This is a most excellent method, both as regards cheapness and purity of product.

Tests.—Solution of baryta, or baryta water, must, after precipitation of the baryta by sulphuric acid, give a filtrate remaining clear when mixed with spirit of wine, and leaving no fixed residue upon evaporation in a platinum crucible.

Uses.—Caustic baryta, being a strong base, precipitates the earths and metallic oxides insoluble in water from the solutions of their salts. In the course of analysis we use it simply to precipitate magnesia. Baryta water may also be used to precipitate those acids which form insoluble compounds with this base; it is applied with this view to effect the detection of carbonic acid, the removal of sulphuric acid, phosphoric acid, &c.

§ 33.

2. Lime ($Ca\,O$).

We use—

a. Hydrate of lime.

b. Lime water.

The former is obtained by slacking pure calcined lime in lumps, in a porcelain dish, with half its weight of water. Hydrate of lime must be kept in a well-stoppered bottle.

To prepare lime water, digest hydrate of lime for some time with cold distilled water, shaking the mixture occasionally; let the undissolved portion of lime subside, decant, and keep the clear fluid in a well-stoppered flask.

Tests.—Lime water must impart a strongly-marked brown tint to turmeric paper, and give a considerable precipitate with carbonate of soda. It speedily loses these properties upon exposure to air, and is thereby rendered totally unfit for analytical purposes.

Uses.—Lime forms with many acids insoluble, with others soluble salts. Lime water may therefore serve to distinguish the former acids, which it precipitates from their solutions, from the latter, which it will of course fail to precipitate. Many of the precipitable acids are thrown down only under certain conditions, *e. g.*, on boiling (citric acid), which affords a ready means of distinguishing between them by altering these conditions. We use lime water in analysis principally to effect the detection of carbonic acid, and also to distinguish between citric acid and tartaric acid. Hydrate of lime is chiefly used to liberate ammonia from the salts of ammonia.

γ. HEAVY METALS AND THEIR OXIDES.

§ 34.

1. Zinc (Zn).

Select zinc of good quality and, above all, perfectly free from arsenic. The method described §§ 131, 10 will serve to detect the presence of the slightest trace of this substance. Fuse the metal, and pour the fused mass in a thin unbroken stream into a large vessel with water. Should the zinc contain arsenic, put the granulated metal into a Hessian crucible, in alternate layers, with ¼ part of nitrate of potassa, heat the crucible gradually until the reaction sets in, and the metal ultimately fuses; granulate now again (*Meillet*).

Uses.—Zinc serves in qualitative analysis for the evolution of hydrogen, and also of arsenetted and antimonetted hydrogen gases (compare §§ 130 and 131); it is occasionally used also to precipitate some metals from their solutions; in which process the zinc simply displaces the other metal ($Cu\,O, S\,O_3 + Zn = Zn\,O, S\,O_3 + Cu$).

§ 35.

2. Iron (Fe).

Iron reduces many metals, and precipitates them from their solutions in the metallic state. We use it especially for the detection of copper, which precipitates upon it with its characteristic color. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, &c., will serve for this purpose.

§ 36.

3. Copper (Cu).

We use copper exclusively to effect the reduction of mercury, which precipitates upon it as a white coating shining with silvery lustre when rubbed. A copper coin scoured with fine sand, or in fact any clean surface of copper, may be employed for this purpose.

§ 37.

4. Hydrate of Teroxide of Bismuth ($Bi\,O_3, H\,O$).*

Preparation.—Dissolve bismuth, freed from arsenic by fusion with hepar sulphuris or nitrate of potassa, in dilute nitric acid; dilute the solution as much as is practicable without producing a permanent precipitate; filter, and evaporate the filtrate to crystallization. Wash the crystals with water containing nitric acid, triturate them with water, add ammonia in excess, and let the mixture digest for some time; then filter, wash, and dry the white precipitate, and keep it for use.

Tests.—Hydrosulphuric acid must throw down from a solution of this reagent in dilute nitric acid, a precipitate insoluble in ammonia and sulphide of ammonium; and, accordingly, the fluid filtered off from the precipitate treated with ammonia must remain perfectly clear upon addition of hydrochloric acid, whilst in that filtered off from the precipitate

* The basic nitrate of teroxide of bismuth of commerce, if perfectly free from arsenic and antimony, may also be used instead of the hydrate of teroxide.

treated with sulphide of ammonium, that acid must only produce a pure white turbidity (sulphur).

Uses.—Teroxide of bismuth, when boiled with alkaline solutions of metallic sulphides, decomposes with the latter, giving rise to the formation of metallic oxides and sulphide of bismuth. It is better adapted to effect decompositions of this kind than oxide of copper, since it enables the operator to judge immediately upon the addition of a fresh portion whether the decomposition is complete or not. It has still another advantage over oxide of copper, viz., it does not, like the latter, dissolve in the alkaline fluid in presence of organic substances; nor does it act as a reducing agent upon reducible oxygen compounds. We use it principally to convert tersulphide and pentasulphide of arsenic into arsenious and arsenic acids, for which purpose oxide of copper is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of suboxide.

b. SULPHUR BASES.

§ 38.

1. Sulphide of Ammonium (NH_4S).

We use in analysis—

a. Colorless proto-sulphide of ammonium.

b. Yellow bi-, ter-, &c., sulphide of ammonium.

Preparation.—Transmit hydrosulphuric acid gas through 3 parts of solution of oxide of ammonium until no further absorption takes place; then add 2 parts more of the same solution of oxide of ammonium. The action of hydrosulphuric acid upon oxide of ammonium gives rise to the formation, first, of NH_4S (NH_4O and $HS = NH_4S$ and HO), then of NH_4S, HS; upon addition of the same quantity of solution of ammonia as has been saturated, the oxide of ammonium decomposes with the double sulphide of ammonium and hydrogen, or, as it is commonly called, the hydrosulphate of sulphide of ammonium, and simple or proto-sulphide of ammonium is formed ($NH_4S, HS + NH_4O = 2(NH_4S) + HO$. The rule, however, is to add only two-thirds of the quantity of solution of ammonia, as it is better the preparation should contain a little hydrosulphate of sulphide of ammonium, than that free ammonia should be present. To employ, as has usually been the case hitherto, hydrosulphate of sulphide of ammonium instead of the simple proto-sulphide, is unnecessary, and simply tends to increase the smell of sulphuretted hydrogen in the laboratory, as the preparation allows that gas to escape when in contact with metallic sulphur acids.

Sulphide of ammonium should be kept in small well-stoppered bottles. It is colourless at first, and deposits no sulphur upon addition of acids. Upon exposure to the air, however, it acquires a yellow tint, owing to the formation of bisulphide of ammonium, which is attended also with formation of ammonia and water:

$$2(NH_4S) + O = NH_4S_2 + NH_3 + HO.$$

Continued action of the oxygen of the air upon the sulphide of ammonium tends at first to the formation of still higher sulphides; but afterwards the fluid deposits sulphur, and, in the end, there remains

nothing in solution but pure ammonia, the whole of the sulphur having separated.

The sulphide of ammonium, which has turned yellow by exposure to the air, may be used for all purposes requiring the employment of yellow sulphide of ammonium: the yellow sulphide may also be expeditiously prepared by digesting the proto-sulphide with some sulphur. All kinds of yellow sulphide of ammonium deposit sulphur, and look turbid and milky on being mixed with acids.

Tests.—Sulphide of ammonium must strongly emit the odor peculiar to it; with acids it must evolve abundance of sulphuretted hydrogen; the evolution of gas may be attended by the separation of a pure white deposit, but no other precipitate must be formed. Upon evaporation and exposure to a red heat on a platinum dish, it must leave no residue. It must not precipitate, nor even render turbid, solution of magnesia or solution of lime (carbonate of ammonia or free ammonia).

Uses.—Sulphide of ammonium is one of the most frequently employed reagents. It serves (*a*) to effect the precipitation of those metals which hydrosulphuric acid fails to throw down from acid solutions, *e. g.* of iron, cobalt, &c. ($NH_4S + FeO, SO_3 = FeS + NH_4O, SO_3$), (*b*) to separate the metallic sulphides thrown down from acid solutions by hydrosulphuric acid, as it dissolves some of them to sulphur salts, as, for instance, the sulphides of arsenic and antimony, &c. (NH_4S, AsS_3, &c.), whilst leaving others undissolved—for instance, sulphide of lead, sulphide of cadmium, &c. The sulphide of ammonium used for this purpose must contain an excess of sulphur, if the metallic sulphides to be dissolved will dissolve only as higher sulphides, as, for instance, SnS, which dissolves with ease only as SnS_2.

From solutions of salts of alumina and sesquioxide of chromium, sulphide of ammonium precipitates hydrates of these oxides, with escape of sulphuretted hydrogen, as the sulphur compounds corresponding to these oxides cannot form in the humid way. [$Al_2O_3, 3SO_3 + 3NH_4S = Al_2O_3, 3HO + 3(NH_4O, SO_3)$]. Salts insoluble in water are thrown down by sulphide of ammonium unaltered from their solutions in acids; thus, for instance, phosphate of lime is precipitated unaltered from its solution in hydrochloric acid.

§ 39.

2. Sulphide of Sodium (NaS).

Preparation.—Same as sulphide of ammonium, except that solution of soda is substituted for solution of ammonia. Keep the fluid obtained in well-stoppered bottles. If required to contain some higher sulphide of sodium, digest it with powdered sulphur.

Uses.—Sulphide of sodium is substituted for sulphide of ammonium to effect the separation of sulphide of copper from sulphur compounds soluble in alkaline sulphides, *e. g.*, from proto-sulphide of tin, as sulphide of copper is not quite insoluble in sulphide of ammonium.

IV. SALTS.

Of the many salts employed as reagents, those of potassa, soda, and ammonia are used principally on account of their acids; salts of soda may, therefore, often be substituted for the corresponding potassa

salts, &c. Thus it is almost always a matter of perfect indifference whether we use carbonate of soda or carbonate of potassa, ferrocyanide of potassium or ferrocyanide of sodium, &c. I have, accordingly, here classified the salts of the alkalies *by their acids*. With the salts of the alkaline earths and those of the oxides of the heavy metals the case is different*; these are not used for their acid, but for their base; we may, therefore, often substitute for one salt of a base another similar one, as *e.g.*, nitrate or acetate of baryta for chloride of barium, &c. For this reason I have classified the salts of the alkaline earths and of the heavy metals *by their bases*.

a. SALTS OF THE ALKALIES.

§ 40.

1. Sulphate of Potassa ($K\,O, S\,O_3$).

Preparation.—Purify sulphate of potassa of commerce by recrystallization, and dissolve 1 part of the pure salt in 12 parts of water.

Uses.—Sulphate of potassa serves to detect and separate baryta and strontia. It is in many cases used in preference to dilute sulphuric acid, which is employed for the same purpose, as it does not, like the latter reagent, disturb the neutrality of the solution.

§ 41.

2. Phosphate of Soda ($2\,Na\,O, H\,O, P\,O_5 + 24$ aq.).

Preparation.—Purify phosphate of soda of commerce by recrystallization, and dissolve one part of the pure salt in 10 parts of water for use.

Tests.—Solution of phosphate of soda must not become turbid when heated with ammonia. The precipitates which solution of nitrate of baryta and solution of nitrate of silver produce in it, must completely, and without effervescence, redissolve upon addition of dilute nitric acid.

Uses.—Phosphate of soda precipitates the alkaline earths, and all metallic oxides, by double affinity. It serves, in the course of analysis, after the separation of the oxides of the heavy metals, as a test for alkaline earths in general; and, after the separation of baryta, strontia, and lime, as a special test for the detection of magnesia; for which latter purpose it is used in conjunction with ammonia, the magnesia precipitating, under these circumstances, as basic phosphate of magnesia and ammonia.

§ 42.

3. Oxalate of Ammonia ($N\,H_4\,O, C_2\,O_3 + $ aq., or $N\,H_4O, \overline{O} + $ aq.).

Preparation.—Dissolve commercial oxalic acid in 20 parts of water, add caustic ammonia, or carbonate of ammonia, until the fluid begins to manifest a slight alkaline reaction; let it stand at rest for 12 hours, filter, and evaporate to crystallization. Purify by recrystallization. Dissolve 1 part of the pure salt in 24 parts of water for use.

Tests.—The solution of oxalate of ammonia must not be precipitated nor rendered turbid by hydrosulphuric acid, nor by sulphide of ammonium.

Uses.—Oxalic acid forms with lime, strontia, baryta, oxide of lead,

and other metallic oxides, insoluble or very difficultly soluble compounds; oxalate of ammonia produces, therefore, in the aqueous solutions of the salts of these bases precipitates of the corresponding oxalates. In analysis it serves principally for the detection of lime.

§ 43.

4. ACETATE OF SODA ($Na\,O, C_4\,H_3\,O_3$ + 6 aq., or $Na\,O, \bar{A}$ + 6 aq.).

Preparation.—Dissolve crystallized carbonate of soda in a little water, add to the solution acetic acid to slight excess, evaporate to crystallization, and purify the salt by recrystallization. For use dissolve 1 part of the salt in 10 parts of water.

Tests.—Acetate of soda when boiled with a solution of molybdate of ammonia mixed with hydrochloric acid must not impart a yellow color to it.

Uses.—The stronger acids in the free state decompose acetate of soda, combining with the base, and setting the acetic acid free. In the course of analysis, acetate of soda is used principally to precipitate phosphate of sesquioxide of iron (which is insoluble in acetic acid) from its solution in hydrochloric acid.

§ 44.

5. CARBONATE OF SODA ($Na\,O, C\,O_2$ + 10 aq.).

Preparation.—Take bicarbonate of soda of commerce, put the powder into a funnel stopped loosely with some cotton, make the surface even, cover it with a disc of difficultly permeable paper with turned-up edges, and wash by pouring small quantities of water on the paper disc, until the filtrate, when acidified with nitric acid, is not rendered turbid by solution of nitrate of silver, nor by solution of chloride of barium. Let the salt dry, and then convert it by gentle ignition into the simple carbonate. This is effected best in a crucible or dish of silver or platinum; but it may be done also in a perfectly clean vessel of cast iron, or, on a small scale, in a porcelain dish. Pure carbonate of soda may be obtained also by repeated recrystallization of carbonate of soda of commerce. For use, dissolve 1 part of the anhydrous salt or 2·7 parts of the crystallized salt in 5 parts of water.

Tests.—Carbonate of soda intended for analytical purposes must be perfectly white. Its solution, when supersaturated with nitric acid, must not be rendered turbid by chloride of barium nor by nitrate of silver; nor must addition of sulphocyanide of potassium impart a red, or boiling with molybdate of ammonia a yellow tint to it; the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, must leave no residue (silicic acid) when redissolved in water.

Uses.—With the exception of the alkalies, carbonate of soda precipitates the whole of the bases, most of them as carbonates, but some also as hydrated oxides. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of soda exhibit a characteristic color, which may lead to the detection of the individual metals which they respectively contain. Solution of carbonate of soda serves, moreover, for the decomposition of many insoluble salts of the alkaline earths or of the metals, more particularly of those

with organic acids. Upon boiling with carbonate of soda, these salts are converted into insoluble carbonates, whilst the acids combine with the soda, and are thus obtained in solution in the form of salts of soda. Carbonate of soda is often used also to saturate free acids.

§ 45.

6. Carbonate of Ammonia (NH_4O, CO_2).

Preparation.—We use for the purposes of chemical analysis purified sesquicarbonate of ammonia, entirely free from any smell of animal oil, such as is prepared on a large sale from chloride of ammonium and carbonate of lime by sublimation. The outer and the inner surface of the mass are carefully scraped. One part of the salt is dissolved by digestion with 4 parts of water, to which one part of solution of caustic ammonia has been added.

Tests.—Pure carbonate of ammonia must completely volatilize. Neither solution of nitrate of baryta nor nitrate of silver, nor sulphuretted hydrogen, must color or precipitate it, after supersaturation with nitric acid.

Uses.—Carbonate of ammonia precipitates, like carbonate of soda, most metallic oxides and earths; it is generally employed in preference to the latter reagent, because it introduces no non-volatile body into the solution. Complete precipitation of many of the oxides takes place only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner, carbonate of ammonia dissolves many hydrated oxides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions many oxides which it precipitates from neutral solutions. (Compare § 51.) We use carbonate of ammonia in chemical analysis principally to effect the precipitation of baryta, strontia, and lime, and the separation of these substances from magnesia, as the latter is not precipitated by this reagent in the presence of salts of ammonia.

§ 46.

7. Bisulphite of Soda ($NaO, 2SO_2$).

Preparation.—Heat 5 parts of copper shreds with 20 parts of concentrated sulphuric acid in a flask, and conduct the sulphurous acid gas evolved, first through a washing bottle containing some water, then into a flask containing 4 parts of purified bicarbonate of soda (§ 44), or 7 parts of crystallized carbonate of soda, and from 20 to 30 parts of water, and which is not much more than half full; continue the transmission of the gas until the evolution of carbonic acid ceases. Keep the solution, which smells strongly of sulphurous acid, in a well-stoppered bottle.

Tests.—Sulphite of soda, when evaporated to dryness with pure sulphuric acid, must leave a residue,* the aqueous solution of which is not altered by hydrosulphuric acid, nor coloured yellow by boiling with a solution of molybdate of ammonia mixed with hydrochloric acid.

Uses.—Sulphurous acid has a great tendency to pass to the state of

* The evaporation is attended with copious evolution of sulphurous acid.

sulphuric acid by absorbing oxygen. It is therefore one of our most powerful reducing agents. Sulphite of soda, which has the advantage of being less readily decomposed than sulphurous acid, acts in an analogous manner as a reducing agent upon acids and higher oxides. We employ it principally to reduce arsenic acid to arsenious acid, chromic acid to sesquioxide of chromium, and sesquioxide of iron to protoxide.

§ 47.

8. Nitrite of Potassa (KO, NO_3).

Preparation.—Fuse 1 part of nitrate of potassa in an iron pan, then add 2 parts of lead, and keep stirring the mixture with an iron rod. The lead oxidizes in a great measure even at a dull red heat, changing to a yellow powder; to oxidize the last remaining particles of the metal, increase the heat to visible redness; in this process the mixture generally takes fire; this, however, is entirely without danger, at least when no more than a quarter of a pound of nitrate of potassa has been used. Let the mass cool, and then treat it with cold water to dissolve out the soluble part; filter this solution, and conduct carbonic acid into the filtrate. This serves to precipitate nearly the whole of the oxide of lead that has passed into the solution; a little hydrosulphuric acid will remove the remainder. Filter again, and evaporate the filtrate to dryness, stirring the mass towards the end of the operation; heat the dry residue to fusion, to destroy any hyposulphite of potassa that may have been formed. Dissolve 1 part of the fused mass in 2 parts of water for use (*Aug. Stromeyer*).

Tests.—Nitrite of potassa must, upon addition of dilute sulphuric acid, copiously evolve nitric oxide gas.

Uses.—Nitrite of potassa is an excellent means to effect the detection and separation of cobalt; in the solutions of which metal it produces a precipitate of nitrite of potassa and sesquioxide of cobalt. It serves also in presence of free acid to liberate iodine from its compounds.

§ 48.

9. Bichromate of Potassa ($KO, 2CrO_3$).

Preparation.—Purify the salt of commerce by recrystallization, and dissolve 1 part of the pure salt in 10 parts of water for use.

Uses.—Chromate of potassa decomposes most of the soluble salts of metallic oxides, by double affinity. Most of the precipitated chromates are very difficultly soluble, and many of them exhibit characteristic colors which lead readily to the detection of the particular metal which they respectively contain. We use bichromate of potassa principally as a test for lead.

§ 49.

10. Antimonate of Potassa ($KO, SbO_5 + 5$ aq.).

Preparation.—Deflagrate in a Hessian crucible 1 part of antimony with 4 parts of nitrate of potassa, and extract the soluble part of the mass with cold water; boil the residue from 2 to 3 hours with 12 parts of water, taking care to replace the evaporating water; this serves to convert the insoluble antimonate of potassa into the soluble

salt. Filter the solution from the small amount of binantimonate which still remains undissolved, and keep for use.

Uses.—Antimonic acid forms with soda a very difficultly soluble salt. Antimonate of potassa affords us, therefore, a means of detecting the presence of soda. For certain conditions and precautions to be observed in its application, I refer to § 89.

§ 50.

11. Molybdate of Ammonia ($N H_4 O, Mo O_3$).

Preparation.—Triturate sulphide of molybdenum with an equal bulk of coarse quartz sand washed with hydrochloric acid, until the mass is reduced to a moderately fine powder (*Brunner*); heat the powder to feeble redness, until the mass has acquired a lemon-yellow color (which after cooling turns whitish). With small quantities, this operation may be conducted in a flat platinum dish, with large quantities, in a muffle properly protected from the ashes; take care to stir the mixture repeatedly during the operation. After cooling, digest the impure molybdic acid produced with solution of ammonia, and let the solution stand at rest for some time in a beaker covered with filtering paper; a yellowish precipitate containing sesquioxide of iron will usually subside. Filter, and keep the perfectly colorless fluid for use. It is sufficiently concentrated if it contains 5 per cent. of molybdic acid. Keep the residuary sulphide of molybdenum for the next operation.

Tests.—Solution of molybdate of ammonia mixed with nitric acid or hydrochloric acid until the precipitate of molybdic acid which forms at first is redissolved, must remain colourless upon boiling. If it acquires a yellow tint, the reagent contains phosphoric acid, and is unfit for use (supposing always, of course, that the hydrochloric or nitric acid was perfectly pure).

Uses.—Molybdic acid forms with phosphoric acid and ammonia a peculiar compound which, in presence of an excess of molybdic acid, is very difficultly soluble in water and acids. The hot solution of this compound has an intensely yellow color. Molybdate of ammonia affords therefore an excellent means to detect minute quantities of phosphoric acid.

§ 51.

12. Chloride of Ammonium ($N H_4, Cl$).

Preparation.—Select sublimed white sal ammoniac of commerce. If it contains iron, it must be purified. For that purpose, add to the solution some sulphide of ammonium, let the precipitate which forms subside, and filter; add hydrochloric acid to the filtrate until the latter manifests a feebly acid reaction; boil the mixture some time, saturate with ammonia, filter, if necessary, and crystallize. For use, dissolve 1 part of the salt in 8 parts of water.

Tests.—Solution of chloride of ammonium must upon evaporation on a platinum knife leave a residue which volatilizes completely upon continued application of heat. Sulphide of ammonium must leave it unaltered. Its reaction must be perfectly neutral.

Uses.—Chloride of ammonium serves principally to retain in solution certain oxides (*e. g.*, protoxide of manganese, magnesia) or salts (*e. g.*,

tartrate of lime), upon the precipitation of other oxides or salts by ammonia or some other reagent. This application of chloride of ammonium is based upon the tendency of the ammonia salts to form double compounds with other salts. Chloride of ammonium serves also to distinguish between precipitates possessed of similar properties; for instance, to distinguish the *basic phosphate of magnesia and ammonia*, which is insoluble in chloride of ammonium, from other precipitates of magnesia. It is used also to precipitate from their solutions in potassa various substances which are soluble in that alkali, but insoluble in ammonia; *e. g.*, alumina, sesquioxide of chromium, &c. In this process the elements of the chloride of ammonium transpose with those of the potassa, and chloride of potassium, water, and ammonia are formed. Chloride of ammonium is applied also as a *special* reagent to effect the precipitation of platinum as ammonio-bichloride of platinum.

§ 52.

13. Cyanide of Potassium (K Cy).

Preparation.—Heat ferrocyanide of potassium of commerce (perfectly free from sulphate of potassa) gently, with stirring, until the crystallization water is completely expelled; triturate the anhydrous mass, and mix 8 parts of the dry powder with 3 parts of perfectly dry carbonate of potassa; fuse the mixture in a covered Hessian or, better still, in a covered iron crucible until the mass is in a faint glow, and appears clear, and a sample of it, taken out with an iron spatula, looks perfectly white. Remove the crucible now from the fire, tap it gently, and let it cool a little until the evolution of gas has ceased; pour the fused cyanide of potassium into a heated crucible-shaped vessel of clean scoured iron or silver, or into a moderately hot Hessian crucible, with proper care, to prevent the running out of any of the minute particles of iron which have separated in the process of fusion and have subsided to the bottom of the crucible. Let the mass now slowly cool in a somewhat warm place. The cyanide of potassium so prepared is exceedingly well adapted for analytical purposes, although it contains carbonate and cyanate of potassa; which latter is upon solution in water transformed into carbonate of ammonia and carbonate of potassa ($K\,O, C_2\,N\,O + 4\,H\,O = K\,O, C\,O_2 + N\,H_4\,O, C\,O_2$). The proper formula for the cyanide of potassium is therefore $5\,K\,Cy + K\,O, Cy\,O + x\,K\,O, C\,O_2$. Keep it in the solid form in a well-stoppered bottle, and for use dissolve 1 part in 4 parts of distilled water, without application of heat.

Tests.—Cyanide of potassium must be of a milk-white color, and quite free from particles of iron or charcoal. It must completely dissolve in water to a clear fluid. It must contain neither silicic acid nor sulphide of potassium; the precipitate which salts of lead produce in its solution must accordingly be of a white color, and the residue which its solution leaves upon evaporation, after previous supersaturation with hydrochloric acid, must completely dissolve in water to a clear fluid.

Uses.—Cyanide of potassium prepared in the manner described produces in the solutions of most of the salts with metallic oxides, precipitates of cyanides of metals or of oxides or carbonates, which are insoluble in water. The precipitated cyanides are soluble in cyanide of potassium, and may therefore be separated from the oxides or carbonates which are

insoluble in cyanide of potassium, by further addition of the reagent. Some of the metallic cyanides redissolve in the cyanide of potassium, even in presence of free hydrocyanic acid and upon boiling, invariably as double cyanides; whilst others combine with cyanogen, forming new radicals, which remain in solution in combination with the potassium. The most common compounds of this nature are cobalticyanide of potassium, and ferro- and ferricyanide of potassium. These differ from the double cyanides of the other descriptions particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may accordingly serve also to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in cyanide of potassium. In the course of analysis, this reagent serves to effect the separation of cobalt from nickel, and also of copper from cadmium.

§ 53.

14. Ferrocyanide of Potassium ($2\,K, C_6\,N_3\,Fe + 3\,aq. = 2\,K, Cfy + 3\,aq.$).

Preparation.—The ferrocyanide of potassium is found in commerce sufficiently pure for the purposes of chemical analysis. 1 part of the salt is dissolved in 12 parts of water for use.

Uses.—Ferrocyanogen forms with most metals compounds insoluble in water, and which frequently exhibit highly characteristic colors. These ferrocyanides are formed when ferrocyanide of potassium is brought into contact with soluble salts of metallic oxides, with chlorides, &c., the potassium changing places with the metals. Ferrocyanide of copper and ferrosesquicyanide of iron exhibit the most characteristic colors of all; ferrocyanide of potassium serves therefore particularly as a test for oxide of copper and sesquioxide of iron.

§ 54.

15. Ferricyanide of Potassium ($3\,K, C_{12}\,N_6\,Fe_2 = 3\,K\,Cfdy$).

Preparation.—Conduct chlorine gas slowly into a solution of 1 part of ferrocyanide of potassium in 10 parts of water, with frequent stirring, until the solution exhibits a fine deep red colour by transmitted light (the light of a candle answers best), and a portion of the fluid produces no longer a blue precipitate, in a solution of sesquichloride of iron, but imparts a brownish tint to it; evaporate the fluid now in a dish to $\frac{1}{4}$ of its weight, and crystallize. The mother liquor will upon further evaporation yield a second crop of crystals equally fit for use as the first. Dissolve the whole of the crystals obtained in 3 parts of water, filter, if necessary; evaporate the solution briskly to half its volume, and crystallize again. Dissolve 1 part of the crystals, which are of a splendid red color, in 10 parts of water for use. The solution, as already remarked, must produce neither a blue precipitate nor a blue color in a solution of sesquichloride of iron.

Uses.—Ferricyanide of potassium decomposes with solutions of metallic oxides in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides, the ferriprotocyanide of iron is more particularly characterized by its color, and we apply ferricyanide of potassium therefore principally as a test for protoxide of iron.

§ 55.

16. SULPHOCYANIDE OF POTASSIUM ($K, C_2 N S_2$ or $K, Cy S_2$).

Preparation.—Mix together 46 parts of anhydrous ferrocyanide of potassium, 17 parts of carbonate of potassa, and 32 parts of sulphur; introduce the mixture into an iron pan provided with a lid, and fuse at a gentle heat; maintain the same temperature until the swelling of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; increase the temperature now, towards the end of the operation, to dull redness, in order to decompose the hyposulphite of potassa which has been formed in this process. Remove the half refrigerated and still soft mass from the pan, pulverize it, and boil with alcohol. Let the alcoholic solution cool, when part of the sulphocyanide of potassium will separate in colorless crystals; to obtain the remainder, distil the alcohol from the mother-liquor. Dissolve 1 part of the salt in 10 parts of water for use.

Uses.—Sulphocyanide of potassium serves for the detection of sesquioxide of iron; it is for that substance at once the most characteristic and delicate test.

b. SALTS OF THE ALKALINE EARTHS.

§ 56.

1. SULPHATE OF BARYTA, CHLORIDE OF BARIUM ($Ba Cl + 2$ aq.).

Preparation.—*a. From heavy spar.* Triturate crude sulphide of barium (§ 32), boil about $\frac{9}{10}$ of the powder with 4 times the quantity of water, and add hydrochloric acid until all effervescence of sulphuretted hydrogen has ceased, and the fluid manifests a feeble acid reaction; add now the remaining $\frac{1}{10}$ part of the sulphide of barium, boil for some time longer, then filter, and let the alkaline fluid crystallize. Dry the crystals, redissolve them in water, and crystallize again.

b. From Witherite. Pour 10 parts of water upon 1 part of Witherite, and gradually add crude hydrochloric acid until the Witherite is almost completely dissolved. Add now a little more finely pulverized Witherite, and heat, with frequent stirring, until the fluid has entirely or very nearly lost its acid reaction; add some baryta water or solution of sulphide of barium, as long as a precipitate forms; filter, evaporate to crystallization; dry the crystals, redissolve them in water, and crystallize again. For use, dissolve 1 part of the chloride of barium obtained in 10 parts of water.

Tests.—Pure chloride of barium must not alter vegetable colors; its solution must not be colored or precipitated by hydrosulphuric acid, nor by sulphide of ammonium. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered from the precipitate formed upon the addition of that reagent leaves not the slightest residue when evaporated on platinum foil.

Uses.—Baryta forms with many acids soluble, with others insoluble compounds. This property of baryta affords us, therefore, a means of distinguishing the former acids which are not precipitated by chloride of barium from the latter, in the solution of the salts of which this reagent

produces a precipitate. The precipitated salts of baryta severally show with other bodies (acids) a different deportment. By subjecting these salts to the action of such bodies, we are therefore enabled to subdivide the group of precipitable acids, and even to detect certain individual acids. This makes chloride of barium one of our most important reagents to distinguish between certain groups of acids, and more especially also for the detection of sulphuric acid.

§ 57.

2. Nitrate of Baryta ($Ba\,O, N\,O_5$).

Preparation.—Pour 12 parts of water upon 1 part of carbonate of baryta, no matter whether Witherite or precipitated by carbonate of soda from solution of sulphide of barium, gradually add dilute nitric acid free from chlorine, and proceed exactly as directed in the preparation of chloride of barium from Witherite. For use, dissolve 1 part of the salt in 15 parts of water.

Tests.—Solution of nitrate of baryta must not be made turbid by solution of nitrate of silver. Other tests the same as for chloride of barium.

Uses.—Nitrate of baryta is used instead of chloride of barium in cases where it is necessary to avoid the presence of a metallic chloride in the fluid.

§ 58.

3. Carbonate of Baryta ($Ba\,O, C\,O_2$).

Preparation.—Dissolve crystallized chloride of barium in water, heat to boiling, and add a solution of carbonate of ammonia mixed with some caustic ammonia, or of pure carbonate of soda, as long as a precipitate forms; let it subside, decant five or six times, transfer the precipitate to a filter, and wash until the washing water is no longer rendered turbid by solution of nitrate of silver. Stir the precipitate with water to the consistence of thick milk, and keep this mixture in a stoppered bottle. It must of course be shaken every time it is required for use.

Tests.—Pure sulphuric acid must precipitate every fixed particle from a solution of carbonate of baryta in hydrochloric acid (compare caustic baryta).

Uses.—Carbonate of baryta completely decomposes the solutions of many metallic oxides, *e. g.*, sesquioxide of iron, alumina; precipitating from them the whole of the oxide as hydrate and basic salt, whilst some other metallic salts are not precipitated by it. It serves therefore to separate the former from the latter, and is an excellent means to effect the separation of sesquioxide of iron and alumina from protoxide of manganese, oxide of zinc, &c., and also from lime and magnesia.

§ 59.

4. Sulphate of Lime ($Ca\,O, S\,O_3$, crystallized $Ca\,O, S\,O_3 + 2\,aq.$).

Preparation.—Digest and shake powdered crystallized gypsum for some time with water; let the undissolved portion subside, decant, and keep the clear fluid for use.

Uses.—Sulphate of lime being a difficultly soluble salt, is a convenient agent in cases where it is wished to apply a solution of a lime salt or of a sulphate of a definite degree of dilution. As dilute solution of a lime salt, it is used for the detection of oxalic acid; whilst as dilute solution of a sulphate it affords an excellent means of distinguishing between baryta, strontia, and lime.

§ 60.

5. CHLORIDE OF CALCIUM ($Ca\ Cl$, crystallized $Ca\ Cl + 6\ aq.$).

Preparation.—Dilute 1 part of crude hydrochloric acid with 6 parts of water, and add to the fluid marble or chalk until the last portion added remains undissolved; add some hydrate of lime, and let the mixture stand for several days in a gentle heat; filter, exactly neutralize the filtrate, concentrate by evaporation, and crystallize. Let the crystals drain, and dissolve 1 part of the salt in 5 parts of water for use.

Tests.—Solution of chloride of calcium must be perfectly neutral, and neither be colored nor precipitated by sulphide of ammonium; nor ought it to evolve ammonia when mixed with hydrate of potassa or hydrate of lime.

Uses.—Chloride of calcium is, in its action and application, analogous to chloride of barium. For, as the latter reagent is used to divide the *inorganic* acids into groups, so chloride of calcium serves in the same manner to effect the separation of the *organic* acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others. And, as is the case with the baryta precipitates, the different conditions under which the various insoluble lime salts are thrown down, enable us to subdivide the group of precipitable acids, and even to detect certain individual acids.

§ 61.

6. SULPHATE OF MAGNESIA ($Mg\ O,\ S\ O_3$, crystallized $Mg\ O,\ S\ O_3,\ H\ O + 6\ aq.$).

Preparation.—Dissolve 1 part of sulphate of magnesia of commerce in 10 parts of water; if the salt is not perfectly pure, subject it to recrystallization.

Uses.—Sulphate of magnesia serves almost exclusively for the detection of phosphoric acid, which it precipitates from aqueous solutions of phosphates in presence of ammonia and chloride of ammonium, in the form of a double salt (basic phosphate of magnesia and ammonia), which is nearly insoluble, and has highly characteristic properties. Sulphate of magnesia is, moreover, employed to test the purity of sulphide of ammonium (see § 38).

c. SALTS OF THE OXIDES OF THE HEAVY METALS.

§ 62.

1. SULPHATE OF PROTOXIDE OF IRON ($Fe\ O,\ S\ O_3$, crystallized $Fe\ O,\ S\ O_3,\ H\ O + 6\ aq.$).

Preparation.—Heat an excess of iron nails free from rust, or of clean iron wire, with dilute sulphuric acid, until the evolution of hydrogen ceases; filter the sufficiently concentrated solution, add a few drops of

dilute sulphuric acid to the filtrate, and allow it to cool. Wash the crystals with water very slightly acidulated with sulphuric acid, dry, and keep for use. The sulphate of protoxide of iron may also be prepared from the solution of sulphide of iron in dilute sulphuric acid, which is obtained in the process of evolving hydrosulphuric acid.

Uses.—Sulphate of protoxide of iron has a great disposition to absorb oxygen, and to be converted into the sulphate of the sesquioxide. It acts therefore as a powerful reducing agent. We employ it principally for the reduction of nitric acid, from which it separates nitric oxide by withdrawing three atoms of oxygen from it. The decomposition of the nitric acid being attended, in this case, with the formation of a very peculiar brownish-black compound of nitric oxide with an undecomposed portion of the salt of the protoxide of iron: this reaction affords a particularly characteristic and delicate test for the detection of nitric acid. Sulphate of protoxide of iron serves, also, for the detection of hydroferricyanic acid, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of the salts of that metal.

§ 63.

2. Sesquichloride of Iron ($Fe_2\ Cl_3$).

Preparation.—Heat in a flask a mixture of 10 parts of water and 1 part of pure hydrochloric acid with small iron nails until no further evolution of hydrogen is observed, even after adding the nails in excess; filter the solution into another flask, and conduct into it chlorine gas, with frequent shaking, until the fluid no longer produces a blue precipitate in solution of ferricyanide of potassium. Heat until the excess of chlorine is expelled. Dilute until the fluid is twenty times the weight of the iron dissolved, and keep the dilute fluid for use.

Tests.—Solution of sesquichloride of iron must not contain an excess of acid; this may be readily ascertained by stirring a sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate, which shaking the vessel and agitating the fluid fail to redissolve. Ferricyanide of potassium must not impart a blue color to it.

Uses.—Sesquichloride of iron serves to subdivide the group of organic acids which chloride of calcium fails to precipitate; as it produces precipitates in solutions of benzoates and succinates, but not in solutions of acetates and formates. The aqueous solutions of the neutral acetate and formate of sesquioxide of iron exhibit an intensely red color; sesquichloride of iron is therefore a useful agent for detecting acetic acid and formic acid. Sesquichloride of iron is exceedingly well adapted to effect the decomposition of phosphates of the alkaline earths (see § 143). It serves also for the detection of hydroferrocyanic acid, with which it produces Prussian blue.

§ 64.

3. Nitrate of Silver ($Ag\ O, N\ O_5$).

Preparation.—Dissolve pure silver in [illegible] nitric acid, evaporate the solution to dryness, and dissolve 1 part [illegible] parts of water.

Tests.—Solution of nitrate of silv[illegible] complete[illegible]tated by

dilute hydrochloric acid, so that the fluid filtered from the precipitated chloride of silver leaves no residue when evaporated on a watch-glass, and is neither precipitated nor colored by hydrosulphuric acid.

Uses.—Oxide of silver forms with many acids soluble, with others insoluble compounds. Nitrate of silver may therefore serve, like chloride of barium, to effect the separation and arrangement of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute nitric acid; chloride, bromide, iodide, and cyanide of silver, &c., are insoluble in that menstruum. Nitrate of silver is therefore a most excellent agent to distinguish and separate from all other acids, the hydracids corresponding to the last enumerated four compounds of silver. Many of the insoluble salts of silver exhibit a peculiar color (chromate of silver, arsenate of silver), or manifest a characteristic deportment with other reagents, or upon the application of heat (formate of silver); nitrate of silver is therefore an important agent for the positive detection of certain acids.

§ 65.

4. Acetate of Lead ($Pb\,O, \overline{A}$, crystallized $Pb\,O, \overline{A} + 3$ aq.).

The best acetate of lead of commerce is sufficiently pure for the purpose of chemical analysis; for use, dissolve 1 part of the salt in 10 parts of water.

Uses.—Oxide of lead forms with a great many acids compounds insoluble in water, which are marked either by peculiarity of color or characteristic deportment. The acetate of lead, therefore, produces precipitates in the solutions of these acids, or of their salts, and essentially contributes to the detection of several of them. Thus, chromate of lead, for instance, is characterized by its yellow colour, phosphate of lead by its peculiar deportment before the blowpipe, and malate of lead by its ready fusibility.

§ 66.

5. Nitrate of Suboxide of Mercury ($Hg_2\,O, N\,O_5$, crystallized $Hg_2\,O, N\,O_5 + 2$ aq.).

Preparation.—Pour 1 part of pure nitric acid on 1 part of mercury, in a porcelain dish, and let the vessel stand twenty-four hours in a cool place; separate the crystals formed from the undissolved mercury and the mother-liquor, and dissolve them in water mixed with one-sixteenth part of nitric acid, by trituration, in a mortar. Filter the solution, and keep the filtrate in a bottle, with metallic mercury covering the bottom of the vessel.

Uses.—Nitrate of suboxide of mercury acts in an analogous manner to the corresponding salt of silver. In the first place, it precipitates many acids, especially the hydracids; and, in the second place, it serves for the detection of several readily oxidizable bodies, *e. g.*, of formic acid, as the oxidation of such bodies, at the expense of the oxygen of the suboxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 67.

6. Chloride of Mercury (Hg Cl).

The chloride of mercury of commerce is sufficiently pure for the purpose of chemical analysis. For use, dissolve 1 part of the salt in 16 parts of water.

Uses.—Chloride of mercury gives with several acids, *e. g.*, with hydriodic acid, peculiarly colored precipitates, and may accordingly be used for the detection of these acids. It is an important agent for the detection of tin, when that metal is in solution in the state of protochloride; if only the smallest quantity of that compound is present, the addition of chloride of mercury in excess to the solution is followed by separation of subchloride of mercury insoluble in water. In a similar manner chloride of mercury serves also for the detection of formic acid.

§ 68.

7. Sulphate of Copper (Cu O, S O_3, crystallized Cu O, S O_3, H O + 4 aq.).

Preparation.—This reagent may be obtained in a state of great purity from the residue remaining in the retort in the process of preparing bisulphite of soda (§ 46), by treating that residue with water, applying heat, filtering, crystallizing, and purifying the salt by recrystallization. For use, dissolve 1 part of the pure crystals in 10 parts of water.

Tests.—Pure sulphate of copper must be completely precipitated from its solutions by hydrosulphuric acid; ammonia and sulphide of ammonium must accordingly leave the filtrate unaltered.

Uses.—Sulphate of copper is employed in qualitative analysis to effect the precipitation of hydriodic acid in the form of subiodide of copper. For this purpose it is necessary to mix the solution of 1 part of sulphate of copper with 2½ parts of sulphate of protoxide of iron, otherwise half of the iodine will separate in the free state. The protoxide of iron changes, in this process, to sesquioxide, at the expense of the oxygen of the oxide of copper, which latter is thus reduced to the state of suboxide. Sulphate of copper is used also for the detection of arsenious and arsenic acid; it serves, likewise, as a test for the soluble ferrocyanides.

§ 69.

8. Protochloride of Tin (Sn Cl, crystallized Sn Cl + 2 aq.).

Preparation.—Reduce English tin to powder by means of a file, or fuse it in a small porcelain dish, remove from the fire, and triturate the fused liquid mass with a pestle until it has passed again to the solid state; boil the powder for some time with concentrated hydrochloric acid in a flask (taking care always to have an excess of tin) until no more hydrogen gas is evolved; dilute the solution with 4 times the quantity of water slightly acidulated with hydrochloric acid, and filter. Keep the filtrate for use in a well-stoppered bottle containing small pieces of metallic tin, or some pure tin-foil. If these precautions are neglected, the protochloride will soon change to bichloride, which will, of course, render the reagent totally unfit for the purpose for which it is intended.

Tests.—Solution of protochloride of tin, when added to a solution of

chloride of mercury, must immediately produce a white precipitate of subchloride of mercury; when treated with hydrosulphuric acid, it must give a dark brown precipitate; it must not be precipitated nor rendered turbid by sulphuric acid.

Uses.—The great tendency of protochloride of tin to absorb oxygen, and thus to form binoxide, or rather bichloride—as the binoxide, in the moment of its formation, decomposes with the free hydrochloric acid present—makes this substance one of our most powerful reducing agents. We employ it in the course of analysis as a test for mercury, and also to effect the detection of gold, for which latter purpose it is previously mixed with some nitric acid, without heat.

§ 70.

9. BICHLORIDE OF PLATINUM ($Pt\,Cl_2$, crystallized $Pt\,Cl_2 + 10$ aq.).

Preparation.—Treat platinum filings purified by boiling with nitric acid, with concentrated hydrochloric acid and some nitric acid, in a narrow-necked flask, and apply a very gentle heat, adding occasionally fresh portions of nitric acid, until the platinum is completely dissolved. Evaporate the solution to dryness on the water-bath, with addition of hydrochloric acid, and dissolve the residue in 10 parts of water for use.

Tests.—Bichloride of platinum must, upon evaporation to dryness in the water-bath, leave a residue which dissolves completely in spirit of wine.

Uses.—Bichloride of platinum forms very sparingly soluble double salts with chloride of potassium and chloride of ammonium, but not so with chloride of sodium; it serves, therefore, to detect ammonia and potassa, and is, indeed, almost our most delicate reagent for the latter substance.

§ 71.

10. SODIO-PROTOCHLORIDE OF PALLADIUM ($Na\,Cl, Pd\,Cl$).

Dissolve 5 parts of palladium in nitrohydrochloric acid (comp. § 70), add 6 parts of pure chloride of sodium, evaporate in the water-bath to dryness, and dissolve 1 part of the residuary double salt in 12 parts of water for use. The brownish solution forms an excellent means of detecting and separating iodine.

§ 72.

11. TERCHLORIDE OF GOLD ($Au\,Cl_3$).

Preparation.—Take fine shreds of gold, which may be alloyed with silver or copper, treat them in a flask with nitrohydrochloric acid in excess, and apply a gentle heat until no more of the metal dissolves. If the gold was alloyed with copper, which is known by the brownish-red precipitate produced by ferrocyanide of potassium in a portion of the solution diluted with water, mix it with solution of sulphate of protoxide of iron in excess; this will reduce the terchloride to metallic gold, which will separate in the form of a fine brownish-black powder; wash the powder in a small flask, and redissolve it in nitrohydrochloric acid; evaporate the solution to dryness on the water-bath, and dissolve the residue in 30 parts of water. If the gold was alloyed with silver, the latter metal remains as chloride upon treating the alloy with nitrohydrochloric acid. In that case evaporate the solution at once to dryness, and dissolve in water for use.

Uses.—Terchloride of gold has a great tendency to yield up its chlorine; it therefore readily converts protochlorides into higher chlorides, protoxides, with the co-operation of water, into higher oxides. These peroxidations are usually indicated by the precipitation of pure metallic gold in the form of a brownish-black powder. In the course of analysis this reagent is used only for the detection of protoxide of tin, in the solutions of which it produces a purple color or a purple precipitate.

V. COLORING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

§ 73.

1. Test Papers.

α. Blue Litmus Paper.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in the 1 part, by repeatedly stirring with a glass rod dipped in very dilute sulphuric acid, until the colour of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of fine unsized paper through it; suspend these slips over threads and leave them to dry. The color of litmus paper must be perfectly uniform, and neither too light nor too dark.

Uses.—Litmus paper serves to detect the presence of free acid in fluids, as acids change its blue color to red. It must be borne in mind, however, that the soluble neutral salts of most of the heavy metallic oxides produce the same effect.

β. Reddened Litmus Paper.

Preparation.—Stir blue solution of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid has just turned distinctly red. Steep slips of paper in the solution, and dry them as in *α*. The [illegible]slips must look distinctly red.

Uses.—Pure alkalies and alkaline earths, and also the sulphides of their metals, restore the blue color of reddened litmus paper; alkaline carbonates and the [illegible] several other weak acids, especially of boracic acid, possess the same property. This reagent serves therefore for the detection of these bodies in general.*

γ. Georgina Paper (*Dahlia Paper*).

Preparation.—Boil the violet-colored petals of *Georgina purpurea* (purple dahlia) in water, or digest them with spirit of wine, and steep slips of paper in the tincture obtained. The latter should be neither more nor less concentrated than is necessary to make the paper, after drying, appear of a fine and light violet blue color. Should the color too much incline to red, this may be remedied by adding a very little ammonia to the tincture.

* Mr. A. S. Taylor has suggested that a very delicate test paper for detecting alkalies may be prepared by steeping slips of paper in an acid infusion of rose petals.

Uses.—Georgina paper is reddened by acids, whilst alkalies impart a beautiful green tint to it. It is therefore an extremely convenient substitute both for the blue and the reddened litmus paper. This reagent, if properly prepared, is a most delicate test both for acids and alkalies. Concentrated solutions of caustic alkalies turn Georgina paper yellow, by destroying the coloring matter.

δ. Turmeric Paper.

Preparation.—Digest and heat 1 part of bruised turmeric root with 6 parts of weak spirit of wine, filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

Uses.—Turmeric paper serves, like reddened litmus paper and dahlia paper, for the detection of free alkalies, &c., as they change its yellow color to brown. It is not quite so delicate a test as the other reagent papers; but the change of color which it produces is highly characteristic, and is very distinctly perceptible in many *colored* fluids; we cannot well dispense, therefore, with this paper. When testing with turmeric paper, it is to be borne in mind that, besides the substances enumerated in β, several other bodies (boracic acid, for instance) possess the property of turning its yellow color to brown-red. It affords an excellent means for the detection of the latter substance.

All test papers are cut into slips, which are kept in small well-closed boxes, or in bottles covered with black paper, as continued action of light destroys the color.

§ 74.

2. Solution of Indigo.

Preparation.—Take from 4 to 6 parts of fuming sulphuric acid, add slowly, and in small portions at a time, 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns deep blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo is thereby destroyed; it is therefore advisable, when dissolving larger quantities of the substance, to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into 20 times the quantity of water, mix, filter, and keep the filtrate for use.

Uses.—Indigo is decomposed by boiling with nitric acid, yellow-colored oxidation products being formed. It serves, therefore, for the detection of nitric acid. Solution of indigo is also well adapted to effect the detection of chloric acid and of free chlorine.

B. REAGENTS IN THE DRY WAY.

I. Fluxes and Decomposing Agents.

§ 75.

1. Mixture of Carbonate of Soda and Carbonate of Potassa ($NaO, CO_2 + KO, CO_2$).

Preparation.—Digest 10 parts of purified bitartrate of potassa in powder with 10 parts of water and 1 part of hydrochloric acid for

several hours on the water-bath, with frequent stirring; put the mass into a funnel with a small filter inserted into the pointed end; let it drain; cover with a disc of rather difficultly permeable filtering paper with upturned edges, and wash by repeatedly pouring upon this small quantities of cold water; continue this washing process until the fluid running off is no longer rendered turbid by solution of nitrate of silver, after addition of nitric acid. Dry the bitartrate of potassa freed in this manner from lime (and phosphoric acid). It is now necessary to prepare pure nitrate of potassa. To effect this, dissolve nitrate of potassa of commerce in half its weight of boiling water, filter the solution into a porcelain or stoneware dish, using a hot funnel, and stir it well with a wooden or porcelain spatula until cold. Transfer the crystalline powder to a funnel loosely stopped with cotton, let it drain, press down tight, make it even at the top, and cover with a double disc of difficultly permeable filtering paper with upturned edges, and pour upon this at proper intervals small portions of water, until the washings are no longer made turbid by solution of nitrate of silver. Empty now the contents of the funnel into a porcelain dish, dry in this vessel, and reduce the mass to a fine powder by trituration. Mix now 2 parts of the pure bitartrate of potassa with 1 part of the pure nitrate of potassa; put the perfectly dry mixture in small portions at a time into a clean-scoured cast-iron pot heated to gentle redness; when the mixture has deflagrated, heat strongly, until a sample taken from the edges gives with water a perfectly colorless solution. Triturate the charred mass with water, filter, wash slightly, and evaporate the filtrate in a porcelain or, better still, in a silver dish, until the fluid is covered with a persistent pellicle. Let the mixture now cool, with constant stirring; put the crystals of carbonate of potassa on a funnel, let them well drain, wash slightly, dry thoroughly in a silver or porcelain dish, and keep the crystals in a well-stoppered bottle. The mother-liquor leaves, upon evaporation, a salt which, though containing traces of alumina and silicic acid, may still be turned to account for many purposes.

Mix 13 parts of the pure carbonate of potassa prepared in the manner just now described, with 10 parts of pure anhydrous carbonate of soda, and keep the mixture in a well-stoppered bottle. The mixture of carbonate of potassa and carbonate of soda may also be prepared by deflagrating 20 parts of pure bitartrate of potassa with 9 parts of pure nitrate of soda, treating with water, and evaporating the solution to dryness.

Tests.—The purity of the mixed salt is tested as directed § 44 (*carbonate of soda*).

Uses.—If silicic acid or silicates are fused with about 4 parts (consequently with an excess) of carbonate of potassa or soda, carbonic acid escapes with effervescence, and a basic alkaline silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate, hydrochloric acid separates the silicic acid as hydrate. If a fixed alkaline carbonate is fused together with sulphate of baryta, strontia, or lime, there are formed carbonates of the alkaline earths and sulphate of the alkali, in which new compounds both the base and the acid of the originally insoluble salt may now be readily detected. However, we do not employ carbonate of potassa separately, nor carbonate of soda, to effect the decomposition of the insoluble silicates and sulphates; but we

apply for this purpose the above-described mixture of both, because this mixture requires a far lower degree of heat for fusion than either of its two components, and thus enables us to conduct the operation over a *Berzelius* lamp, or over a simple gas lamp. The fusion with alkaline carbonates is invariably effected in a platinum crucible, provided no reducible metallic oxides be present.

§ 76.

2. Hydrate of Baryta (BaO, HO).

Preparation.—The crystals of baryta prepared in the manner directed § 32, are heated gently in a silver or platinum dish, until the water of *crystallization* is completely expelled. The residuary white mass is pulverized, and kept for use in a well-closed bottle.

Uses.—Hydrate of baryta fuses at a gentle red heat without losing its water. Upon fusing silicates together with about 4 parts of hydrate of baryta, a basic silicate of baryta is formed, and the oxides are liberated. If the fused mass is treated with hydrochloric acid, the solution evaporated to dryness, and the residue digested with hydrochloric acid, the silicic acid is left behind, and the oxides are obtained in solution in the form of chlorides. We use hydrate of baryta as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to the carbonate or nitrate of baryta, since it does not require a very high temperature for its fusion, as is the case with the carbonate, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the nitrate. The operation is conducted in silver or platinum crucibles.

§ 77.

3. Fluoride of Calcium ($CaFl$).

Take fluor-spar as pure as can be procured, and more particularly free from alkalies, reduce to fine powder, and keep this for use.

Uses.—Fluoride of calcium applied in conjunction with sulphuric acid, serves to effect the decomposition of silicates insoluble in acids, and more especially to detect the alkalies which they contain. Compare Section III. *Silicic acid*, § 150.

§ 78.

4. Nitrate of Soda (NaO, NO_5).

Preparation.—Neutralize pure nitric acid with pure carbonate of soda exactly, and evaporate to crystallization. Dry the crystals thoroughly, triturate, and keep the powder for use.

Tests.—A solution of nitrate of soda must not be made turbid by solution of nitrate of silver or nitrate of baryta, nor precipitated by carbonate of soda.

Uses.—Nitrate of soda serves as a very powerful oxidizing agent, by yielding oxygen to combustible substances when heated with them. We use this reagent principally to convert several metallic sulphides, and more particularly the sulphides of tin, antimony, and arsenic, into oxides and acids; and also to effect the rapid and complete combustion of organic substances; for the latter purpose, however, nitrate of ammonia

is in many cases preferable; this latter reagent is prepared by saturating nitric acid with carbonate of ammonia.

II. Blowpipe Reagents.

§ 79.

1. Carbonate of Soda ($Na\,O, C\,O_2$).

Preparation.—See § 44.

Uses.—Carbonate of soda serves, in the first place, to promote the reduction of oxidized substances in the inner flame of the blowpipe. In fusing it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. It co-operates in this process also chemically by the transposition of its constituents (according to *R. Wagner*, in consequence of the formation of cyanide of sodium). If the quantity operated upon was very minute, the reduced metal is often found in the pores of the charcoal. In such cases, the parts surrounding the little cavity which contained the sample are dug out with a knife, and triturated in a small mortar; the charcoal is then washed off from the metallic particles, which now become visible either in the form of powder or as small flat spangles, according to the nature of the particular metal or metals present.

Carbonate of soda serves, in the second place, as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing carbonate of soda. A few only of the bases dissolve in fusing carbonate of soda, but acids dissolve in it with facility. Carbonate of soda is, moreover, applied as a decomposing agent and flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, the newly formed sulphate of soda being reduced at the same time to sulphide of sodium; and to effect the decomposition of sulphide of arsenic, with which it forms a double sulphide of arsenic and sodium, and arsenite or arsenate of soda, thus converting it to a state which permits its subsequent reduction by hydrogen. Finally, carbonate of soda is the most sensitive reagent in the dry way for the detection of manganese, since when fused in the outer flame of the blowpipe together with a substance containing manganese, it produces a green opaque bead, owing to the formation of manganate of soda.

§ 80.

2. Cyanide of Potassium (K Cy).

Preparation.—See § 52.

Uses.—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way; indeed it excels in its action almost all other reagents of the same class, and separates the metals not only from most oxygen compounds, but also from sulphur compounds: this reduction is attended in the former case with formation of cyanate of potassa, by the absorption of oxygen, and in the latter case with formation of sulphocyanide of potassium. By means of this reagent we may effect the reduction of metals from their compounds with the greatest possible facility; thus we may, for instance, produce metallic antimony from antimonious acid or from sulphide of antimony, metallic iron from sesquioxide of iron, &c.

The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit lamp. Cyanide of potassium is a most valuable and important agent to effect the reduction of arsenites and arsenates, and more particularly of tersulphide of arsenic (see § 131). Cyanide of potassium is equally important as a blowpipe reagent. Its action is exceedingly energetic; substances like binoxide of tin, bisulphide of tin, &c., the reduction of which by means of carbonate of soda requires a tolerably strong flame, are reduced by cyanide of potassium with the greatest facility. In blowpipe experiments we invariably use a mixture of equal parts of carbonate of soda and cyanide of potassium; the admixture of carbonate of soda is intended here to check in some measure the excessive fusibility of the cyanide of potassium. This mixture of cyanide of potassium with carbonate of soda, besides being a far more powerful reducing agent than the simple carbonate of soda, has, moreover, this great advantage over the latter, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 81.

3. Biborate of Soda (*Borax*) ($NaO, 2\,BO_3$, crystallized + 10 aq.).

The purity of commercial borax may be tested by adding to its solution carbonate of soda, or after previous addition of nitric acid, solution of nitrate of baryta or of nitrate of silver. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the fluid turbid, recrystallization is necessary. The pure crystallized borax is exposed to a gentle heat, in a platinum crucible, until it ceases to swell; when cool, it is pulverized and kept for use.

Uses.—Boracic acid manifests a great affinity for oxides when brought into contact with them in a state of fusion. This affinity enables it, in the first place, to combine directly with oxides; secondly, to expel weaker acids from their salts; and, thirdly, to predispose metals, sulphides, and haloid compounds to oxidize in the outer flame of the blowpipe, that it may combine with the oxides. Most of the thus produced borates fuse readily, even without the aid of a flux, but far more so in conjunction with borate of soda; the latter salt acts in this operation either as a mere flux, or by the formation of double salts. Now, in the biborate of soda we have both free boracic acid and borate of soda; the union of these two substances renders it one of our most important blowpipe reagents. In the process of fluxing with borax, we usually select platinum wire for a support; the loop of the wire is moistened or heated to redness, then dipped into the powder, and exposed to the outer flame; a colourless bead of fused borax is thus produced. A small portion of the substance under examination is then attached to the bead, by bringing the latter into contact with it, either whilst still hot or having previously moistened it. The bead with the sample of the substance intended for analysis adhering to it, is now exposed to the blowpipe flame, and the phenomena to the manifestation of which this process gives rise are carefully observed and examined. The following points ought to be more particularly watched:—(1) Whether or not the sample under examination dissolves to a transparent bead, and whether or not the bead retains its transparency on cooling; (2) whether the bead exhibits a dis-

tinct color, which in many cases at once clearly indicates the individual metal which the analysed compound contains, as is the case, for instance, with cobalt; and (3) whether the bead manifests the same or a different deportment in the outer and in the inner flame. Phenomena of the latter kind arise from the ensuing reduction of higher to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

§ 82.

4. PHOSPHATE OF SODA AND AMMONIA (*Microcosmic Salt*) ($Na\,O, N\,H_4\,O, H\,O, P\,O_5$, crystallized + 8 aq.).

Preparation.—Heat to boiling 6 parts of phosphate of soda and 1 part of pure chloride of ammonium with 2 parts of water, and let the solution cool. Free the crystals produced of the double phosphate of soda and ammonia by recrystallization from the chloride of sodium which adheres to them. Dry the purified crystals, and pulverize them for use.

Uses.—When phosphate of soda and ammonia is subjected to the action of heat, the ammonia escapes with the water of crystallization, and readily fusible metaphosphate of soda is left behind. The action of microcosmic salt is quite analogous to that of biborate of soda. We prefer it, however, in some cases, to borax as a solvent or flux, the beads which it forms with many substances being more beautifully and distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop of the wire must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed in the preceding paragraph.

§ 83.

5. NITRATE OF PROTOXIDE OF COBALT ($Co\,O, N\,O_5$, crystallized + 5 aq.).

Preparation.—Fuse in a Hessian crucible 3 parts of bisulphate of potassa, and add to the fused mass, in small portions at a time, 1 part of well roasted cobalt ore (the purest zaffre you can procure) reduced to fine powder. The mass thickens, and acquires a pasty consistence. Heat now more strongly, until it has become more fluid again, and continue to apply heat until the excess of sulphuric acid is *completely* expelled, and the mass accordingly no longer emits white fumes. Remove the fused mass now from the crucible with an iron spoon or spatula, let it cool, and reduce it to powder; boil this with water until the undissolved portion presents a soft mass; then filter the rose-red solution, which is free from arsenic and nickel, and mostly also from iron, and remove the copper, &c., from the filtrate by means of hydrosulphuric acid. Filter again, and evaporate the filtrate, with addition of some chlorine water, until it is much concentrated. Mix the concentrated filtrate now with a hot saturated solution of binoxalate of potassa, and let the mixture stand at a gentle heat until the fluid appears colorless. Wash the precipitated oxalate of protoxide of cobalt thoroughly, dry, and heat to redness in a covered platinum or porcelain crucible. This decomposes the oxalate into water and carbonic acid, which escapes, and metallic cobalt, which is left behind. Dissolve a portion of the latter in nitric acid, taking care to avoid a large excess of the solvent; evaporate the solution in the water-bath to dryness, and dissolve 1 part of the residue in 10 parts of water for use.

Tests.—Solution of nitrate of protoxide of cobalt must be free from other metals, and especially also from salts of the alkalies; when precipitated with sulphide of ammonium and filtered, the filtrate must, upon evaporation on platinum, leave no fixed residue.

Uses.—Protoxide of cobalt forms, upon ignition with certain infusible bodies, peculiarly colored compounds, and may accordingly serve for the detection of these bodies (oxide of zinc, alumina, and magnesia; see Section III.).

§ 84.

6. Chloride of Silver ($Ag\,Cl$).

Preparation.—Precipitate solution of nitrate of silver with hydrochloric acid; wash the precipitate, mix it with water to a thick pulp, and keep in a small bottle for use.

Uses.—Chloride of silver has lately been recommended by *Gericke* as a means of making the colorations more distinct and lasting which certain bodies, upon exposure to the inner blowpipe flame, impart to the outer flame. I can from my own experience confirm the results arrived at by *Gericke.* The action of the chloride of silver is owing to the circumstance that this compound loses its chlorine only gradually upon exposure to heat, and gives rise accordingly for a certain time to the formation of metallic chlorides, which it is well known [illegible]t more distinct colorations to flame than any other class of salts. [illegible]tinum wire would speedily be rendered unfit for use by the reduc[illegible]r, thin iron wire is employed; every operation requires a new loop.

SECTION [illegible]

ON THE DEPORTMENT OF BODIES WITH REAGENTS.

§ 85.

I stated in my introductory remarks that the operations and experiments of qualitative analysis have for their object the conversion of the *unknown* constituents of any given compound into forms of which we *know* the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the several constituents of which the analysed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends upon the greater or less degree of certainty with which they lead to definite results, no matter whether of a positive or negative nature. But as a question does not render us any the wiser if we do not know the language in which the answer is returned, so, in like manner, will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of our reagents upon the substance examined.

Before we can therefore proceed to enter upon the practical investiga-

tions of analytical chemistry, it is indispensable that we should *really* possess the most perfect knowledge of the deportment, relations, and properties of the new forms into which we intend to convert the substances we wish to analyse. Now, this perfect knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds and the manifestation of the various reactions; and, in the second place, in a distinct impression of the color, form, and physical properties which characterize the new compound. This section of the work demands therefore not only the most careful and attentive study, but requires moreover that the student should *examine and verify by actual experiment every fact asserted in it.*

The method usually adopted in elementary works on chemistry is to treat of the various substances and their deportment with reagents individually and separately, and to point out their characteristic reactions. I have, however, in the present work, deemed it more judicious and better adapted to its elementary character, to arrange those substances which are in many respects analogous into groups, and thus, by comparing their analogies with their differences, to place the latter in the clearest possible light.

A.—Deportment and Properties of the Metallic Oxides and of their Radicals.

§ 86.

Before proceeding to the special study of the several metallic oxides, I give here a general view of the whole of them, classified in groups—showing *which* oxides belong to each group. The *grounds* upon which the classification has been arranged will appear from the special consideration of the several groups.

First group—

Potassa, soda, ammonia (lithia).

Second group—

Baryta, strontia, lime, magnesia.

Third group—

Alumina, sesquioxide of chromium (glucina, thorina, noria, yttria, terbia, erbia, zirconia—earths; oxides of cerium, lanthanium, didymium; oxide of titanium and titanic acid; tantalic acid, niobic acid).

Fourth group—

Oxides of *zinc, manganese, nickel, cobalt, iron* (uranium).

Fifth group—

Oxides of *silver, mercury, lead, bismuth, copper, cadmium* (palladium, rhodium, osmium, ruthenium).

Sixth group—

Oxides and acids of *antimony, tin, arsenic, gold, platinum* (iridium, molybdenum, tellurium, tungsten, vanadium).

Of these metallic oxides only those printed in *italics* are found extensively and in large quantities in that portion of the earth's crust which is accessible to our investigations; these, therefore, are most important to chemistry, arts and manufactures, agriculture, pharmacy, &c. &c.; and these therefore we shall dwell upon at greater length. The more important among the remainder are more briefly considered in supplementary paragraphs; and the less important ones are altogether

omitted. The deportment of the metals I have given only in the case of those that are more frequently met with in analytical operations in the metallic state.

§ 87.

FIRST GROUP.

Potassa, Soda, Ammonia.

Properties of the group.—The alkalies are readily soluble in water, as well in the pure or caustic state as in the form of sulphides, carbonates, and phosphates. Accordingly they do not precipitate one another in the pure state, nor as carbonates or phosphates, nor are they precipitated by hydrosulphuric acid under any condition whatever. The solutions of the pure alkalies, as well as of their sulphides and carbonates, restore the blue color of reddened litmus-paper, and impart an intensely brown tint to turmeric paper.

Special Reactions.

§ 88.

a. Potassa (K O).

1. Potassa and its hydrate and salts are not volatile at a faint red-heat. Potassa and its hydrate deliquesce in the air; the oily liquids formed do not solidify by absorption of carbonic acid.

2. Nearly the whole of the salts of potassa are readily soluble in water. They are colorless, if the constituent acid is so. The neutral salts of potassa with strong acids do not alter vegetable colors. Carbonate of potassa crystallizes with difficulty, and deliquesces in the air. Sulphate of potassa is anhydrous, and suffers no alteration in the air.

3. *Bichloride of platinum* produces in the neutral and acid solutions of the salts of potassa a yellow, crystalline, heavy precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (*potassio-bichloride of platinum*) ($K\,Cl, Pt\,Cl_2$). In concentrated solutions this precipitate separates immediately upon the addition of the reagent: in dilute solutions it forms only after some time, often after a *considerable* time. Very dilute solutions are not precipitated by the reagent. The precipitate consists of octahedrons discernible under the microscope. Alkaline solutions must be acidified with hydrochloric acid before the bichloride of platinum is added. The precipitate is difficultly soluble in water; the presence of free acids does not greatly increase its solubility; it is insoluble in alcohol. Bichloride of platinum is therefore a particularly delicate test for salts of potassa dissolved in spirit of wine. The best method of applying this reagent is to evaporate the aqueous solution of the potassa salt with bichloride of platinum nearly to dryness on the water-bath, and to pour a little water on the residue, or, better still, some spirit of wine, provided no substances insoluble in that menstruum be present: the potassio-bichloride of platinum is left undissolved. Care must be taken not to confound this double salt with ammonio-bichloride of platinum, which greatly resembles it (see §§ 90, 4).

4. *Tartaric acid* produces in neutral or alkaline* solutions of salts of potassa—a white, quickly subsiding, *granular* crystalline precipitate of

* In the case of alkaline solutions, the reagent must be added until the fluid shows a strongly acid reaction.

BITARTRATE OF POTASSA ($K O, H O, C_8 H_4 O_{10}$). In concentrated solutions this precipitate separates immediately; in dilute solutions often only after the lapse of some time. Vigorous shaking or stirring of the fluid promotes its formation considerably. Very dilute solutions are not precipitated by this reagent. Free alkalies and free mineral acids dissolve the precipitate; it is difficultly soluble in cold, but pretty readily soluble in hot water. In the case of acid solutions, the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with soda or carbonate of soda, before we can proceed to test for potassa with tartaric acid.

5. If a salt of potassa, more particularly chloride of potassium, is held on a platinum wire in the apex of the *inner blowpipe flame*, the outer flame acquires a VIOLET color. The tint which phosphate and borate of potassa impart to the outer blowpipe flame is scarcely perceptible. Presence of a salt of soda completely obscures the reaction. Decrepitating salts are pulverized and made to adhere to the wire with water. Addition of chloride of silver promotes the reaction in the case of nitrate, carbonate, &c., of potassa (§ 84).

6. If a salt of potassa (more particularly chloride of potassium) is heated with a small quantity of water, alcohol (burning with colorless flame) added, heated, and then kindled, the flame appears VIOLET. The presence of soda obscures this reaction.

§ 89.

b. SODA ($Na O$).

1. Soda and its hydrate and salts present in general the same deportment and properties as potassa and its corresponding compounds. The oily fluid which soda forms by deliquescing in the air, resolidifies speedily by absorption of carbonic acid. Carbonate of soda crystallizes readily; the tabular crystals ($Na O, C O_2 + 10$ aq.) effloresce rapidly when exposed to the air. The same applies to the prismatic crystals of sulphate of soda ($Na O, S O_3 + 10$ aq.).

2. *Antimonate of potassa* produces in neutral or feebly alkaline solutions of salts of soda a white, crystalline precipitate of METANTIMONATE OF SODA ($Na O, Sb O_5 + 7$ aq.). Vigorous shaking of the mixture promotes its formation. If the fluid, after the addition of the reagent, be stirred with a glass rod, moving the latter along the sides of the vessel, the lines described will, even in very dilute solutions, speedily become visible, since the precipitate forms first on the parts rubbed by the rod. If the precipitate separates slowly, it consists of well-formed microscopic quadrilateral octahedrons. The presence of neutral salts of potassa interferes only slightly with the formation of the precipitate; but carbonate of potassa, when present in larger proportion, wholly prevents its separation from more dilute solutions. In cases, therefore, where the solution under examination contains this salt, it is necessary to precede the application of the antimonate of potassa by addition of hydrochloric or acetic acid until the reaction of the solution remains only feebly alkaline. Acid solutions must first be neutralized with potassa, since otherwise the reagent would suffer decomposition, and hydrated antimonic acid or acid antimonate of potassa be precipitated from it.

3. Salts of soda (more particularly chloride of sodium), when exposed

on a platinum wire to the *inner blowpipe flame*, color the outer flame INTENSELY YELLOW. This reaction remains clearly perceptible, even if the soda contains a considerable admixture of potassa. Chloride of silver promotes the reaction in the case of some, but not of all salts of soda.

4. If a salt of soda (more particularly chloride of sodium) is heated with a small quantity of water, *alcohol* added, and the latter heated and then kindled, the flame appears strongly YELLOW. The presence of a salt of potassa does not impair the distinctness of this reaction.

5. *Bichloride of platinum* produces no precipitate in solutions of salts of soda; *tartaric acid* only when a highly concentrated solution of soda or carbonate of soda is mixed with a saturated solution of tartaric acid in excess. The bulky precipitate of BITARTRATE OF SODA which in that case separates, consists of small needles and columns, and requires only 12 parts of cold water for its solution; it is not likely, therefore, to be confounded with the granular crystalline precipitate of bitartrate of potassa.

§ 90.

c. AMMONIA ($N H_4 O$).

1. Anhydrous ammonia ($N H_3$) is gaseous at the common temperature; but we have most frequently to deal with it in its aqueous solution, in which it betrays its presence at once by its penetrating odor. It is expelled from this solution by the application of heat. It may be assumed that the solution contains it as oxide of ammonium ($N H_4 O$) (see § 31).

2. All the salts of ammonia are volatile at a high temperature, either with or without decomposition. Most of them are readily soluble in water. The solutions are colorless. The neutral compounds of ammonia with strong acids do not alter vegetable colors.

3. If salts of ammonia are triturated together with *hydrate of lime*, best with the addition of a few drops of water, or are, either in a solid form or in solution, heated with solution of potassa or of soda, the ammonia is liberated in the gaseous state, and betrays itself (1) by its characteristic *odor*; (2) by its *reaction* on moistened test-papers; and (3) by giving rise to the formation of *white fumes*, when any object (*e. g.*, a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought in contact with it. These fumes arise from the formation of solid ammoniacal salts produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of a mistake. In cases where the quantity of ammonia present is only very small, the best way of testing the alkaline reaction of the fumes is to cover a small beaker containing the mixture with a watch-glass, having a slip of moistened turmeric or reddened litmus-paper attached to the convex side, to place it on a hot slab, and observe, after a few minutes, whether the test-paper has changed color.

4. *Bichloride of platinum* shows the same deportment with salts of ammonia as with salts of potassa; the yellow precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM ($N H_4 Cl, Pt Cl_2$) is, however, of a somewhat lighter color than potassio-bichloride of platinum. It consists, like the corresponding potassium compound, of octahedrons, discernible under the microscope.

5. *Tartaric acid* added in excess to a solution of ammonia or carbonate

of ammonia, produces a white crystalline precipitate of BITARTRATE OF AMMONIA ($N H_4 O, C_8 H_4 O_{10}$). In concentrated solutions this precipitate forms immediately; in dilute solutions only after some time. The solutions of other ammoniacal salts (chloride of ammonium, nitrate of ammonia, &c.) are not precipitated by this reagent, even when highly concentrated; or a trifling precipitate only separates after long standing. Bitartrate of ammonia comports itself with solvents like the corresponding salt of potassa; however, it is somewhat more readily soluble in water and acids than the latter.

6. If a solution of *potassio-iodide of mercury*,* containing much caustic potassa, is mixed with a fluid containing ammonia or an ammoniacal salt, a reddish-brown precipitate of hydrated TETRAHYDRARGYRO-IODIDE OF AMMONIUM ($N Hg_4 I + 2 H O$): $4 (Hg I, K I) + 3 K O + N H_3 = (N Hg_4 I + 2 H O) + 7 K I + H O$, separates immediately or upon application of a gentle heat. This precipitate redissolves in presence of an excess of ammoniacal salts; but reprecipitates upon further addition of potassa; it is soluble also in solution of iodide of potassium, but the less so the more free potassa happens to be present. When a considerable excess of potassa exists, therefore, the precipitate is insoluble in iodide of potassium. Presence of chlorides of the alkali metals, or of salts of potassa and soda, does not interfere with the reaction; but cyanides and sulphides of the alkali metals prevent it. This reaction was first pointed out by *Nessler;* it is not required for ordinary analyses, but is extremely valuable in cases where the presence of minute traces of ammoniacal salts are to be detected. I have found it to give distinct indications of the presence of ammonia in solutions of 0·00001 gramme of chloride of ammonium in 1 cubic centimètre of water.

§ 91.

Recapitulation and remarks.—The salts of potassa and soda are not volatile at a moderate red heat, whilst the salts of ammonia volatilize readily; the latter may therefore be easily separated from the former by ignition. The expulsion of *ammonia* from its compounds, by hydrate of lime, affords the surest means of ascertaining the presence of this substance. Salts of potassa can be detected *positively* only after the removal of the ammoniacal salts which may be present, since both classes of salts manifest the same or a similar deportment with bichloride of platinum and tartaric acid. After the removal of the ammonia, the *potassa* is clearly and positively characterized by either of these two reagents. The most simple way of detecting the potassa in the two difficulty-soluble compounds that have come under our consideration here—viz., the potassio-bichloride of platinum and bitartrate of potassa—is to decompose these salts by ignition; the former, thereupon, yields the potassa in the form of chloride of potassium, the latter in the form of carbonate of potassa. With respect to *soda*, the yellow tint which its salts impart to the blowpipe flame and to the flame of alcohol, is a safe and mostly in itself sufficient proof of its presence, provided always no other bodies be present besides salts of fixed alkalies. In form of chlorides, $\frac{1}{100}$th part of soda may by this means be detected in presence of potassa. Anti-

* To prepare this reagent, digest at a gentle heat 2 grammes of iodide of potassium, and 3 grammes of iodide of mercury, in 5 cub. cent. of water; add 20 cub. cent. of water, let the mixture stand for some time, then filter; add to the filtrate 30 cub. cent. of pure concentrated solution of potassa (1 : 4); and, should a precipitate form, let this settle; decant, and use the clear decanted fluid.

monate of potassa also gives decisive results when no other bases besides soda or potassa are present, and especially if these latter are present as chlorides or nitrates. Even from very dilute solutions of salts of soda, antimonate of potassa added in excess will, after twelve hours' standing, throw down antimonate of soda, the crystals of which may always be readily and distinctly recognised under the microscope by their form—quadrilateral octahedrons.

§ 92.

SUPPLEMENT TO THE FIRST GROUP.

LITHIA (Li O).

Lithia dissolves with difficulty in water; it does not attract moisture from the air. Most of its salts are soluble in water; some of them are deliquescent (chloride of lithium). Carbonate of lithia is difficultly soluble, particularly in cold water. *Phosphate of soda* produces, in not over dilute solutions of salts of lithia, upon boiling, a heavy white crystalline precipitate of basic phosphate of lithia (3 Li O, P O_5 + aq.). From very dilute solutions of lithia the same basic phosphate is obtained by adding phosphate of soda and one or two drops of solution of soda to the solution, evaporating the mixed fluid to dryness, and treating the residue with water. The basic phosphate of lithia obtained is sparingly soluble in water, and still less so in ammoniated water; it dissolves much more readily in water containing salts of ammonium. It is immediately dissolved by acids; addition of ammonia produces no precipitate in somewhat dilute acid solutions in the cold, but upon boiling, a precipitate separates. The basic phosphate of lithia fuses before the blowpipe, and gives upon fusion with carbonate of soda on the platinum wire a clear bead; when fused upon charcoal, it is absorbed by the pores of the latter body (another difference between it and the phosphate of the alkaline earths). *Tartaric acid* and *bichloride of platinum* fail to precipitate even concentrated solutions of salts of lithia; but in a solution of chloride of potassium containing chloride of lithium, bichloride of platinum readily produces a precipitate containing lithia (*Jenzsch*). If a salt of lithia (more particularly chloride of lithium) is exposed on a platinum wire to the *inner blowpipe flame*, the outer flame shows a strong CARMINE tint. Presence of salts of soda (but not of salts of potassa) conceals this reaction. Addition of chloride of silver promotes it in the case of some, but not of all salts of lithia. If *spirit of wine* is poured over a salt of lithia (more particularly chloride of lithium), and then kindled, the flame appears of a CARMINE colour; presence of salts of soda conceals this reaction.

To detect lithia in presence of potassa and soda, convert the bases into dry chlorides; treat them, after addition of a drop of hydrochloric acid, with a mixture of absolute alcohol and anhydrous ether; filter, distil, and treat the residue remaining after distillation again with the said mixture, after previous addition of a drop of hydrochloric acid; filter, concentrate the filtrate by evaporation, and then set fire to the concentrated fluid. A carmine-coloured flame indicates the presence of lithia. The residue remaining after evaporation of the alcohol must dissolve in water to a clear fluid; the solution must not be precipitated by carbonate of ammonia (lime, strontia), and must give the above-mentioned reaction with phosphate of soda. This method is based upon the insolubility of chloride

of potassium, and chloride of sodium in absolute alcohol and ether, in which chloride of lithium readily dissolves.

§ 93.

SECOND GROUP.

BARYTA, STRONTIA, LIME, MAGNESIA.

Properties of the group.—The alkaline earths are soluble in water in the pure (caustic) state and as sulphides. Magnesia, however, dissolves but very sparingly in water. The solutions manifest alkaline reaction; the alkaline reaction of magnesia is most clearly apparent when that earth is laid upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water. The solutions of the salts of the alkaline earths are therefore precipitated by alkaline carbonates and phosphates, whilst hydrosulphuric acid fails to precipitate them under any condition. This deportment distinguishes the oxides of the second group from those of the first. The alkaline earths and their salts are non-volatile and colorless; their solutions are not precipitated by sulphide of ammonium, nor by carbonate of baryta.

Special Reactions.

§ 94.

a. BARYTA ($Ba\,O$).

1. Caustic baryta is pretty readily soluble in hot water, but rather difficultly so in cold water; it dissolves easily in dilute hydrochloric or nitric acid. Hydrate of baryta does not lose its water upon ignition.

2. Most of the salts of baryta are insoluble in water. The soluble salts do not affect vegetable colors, and are decomposed upon ignition, with the exception of chloride of barium. The insoluble salts dissolve in dilute hydrochloric acid, except the sulphate of baryta. Nitrate of baryta and chloride of barium are insoluble in alcohol, and do not deliquesce in the air. Concentrated solutions of baryta are precipitated by hydrochloric or nitric acid added in large proportions, as chloride of barium and nitrate of baryta are not soluble in the aqueous solutions of the said acids.

3. *Ammonia* (free from carbonic acid) produces no precipitate in the aqueous solutions of salts of baryta; *potassa* or *soda* (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of CRYSTALS OF BARYTA ($Ba\,O, H\,O + 8$ aq.) produced by potassa or soda.

4. *Alkaline carbonates* throw down from solutions of baryta CARBONATE OF BARYTA ($Ba\,O, C\,O_2$) in the form of a white precipitate. When carbonate of ammonia is used as the precipitant, or if the solution was previously acid, complete precipitation takes place only upon heating the fluid. In chloride of ammonium the precipitate is soluble to a trifling yet clearly perceptible extent; in very dilute solutions of baryta, therefore, which contain much chloride of ammonium, carbonate of ammonia produces no precipitate.

5. *Sulphuric acid* and all the soluble *sulphates*, also solution of sulphate of lime, produce even in very dilute solutions of baryta, a

heavy, finely pulverulent, white precipitate of SULPHATE OF BARYTA ($Ba\ O, S\ O_3$), which is insoluble or very difficultly soluble in dilute acids, alkalies, and salts of ammonia. As a rule, this precipitate is formed immediately upon the addition of the reagent; from highly dilute solutions, however, especially when strongly acid, it separates only after some time. Sulphate of baryta is completely decomposed by fusion with carbonates of the alkalies—less readily and less completely by boiling with solution of carbonate of soda and carbonate of potassa. The decomposition leads to the formation of sulphates of the alkalies, which are soluble in water, and carbonate of baryta, which is insoluble in that fluid. Digestion with solution of carbonate of ammonia in the cold fails to effect the decomposition of sulphate of baryta, as also boiling with a solution of 1 part of carbonate and 3 parts of sulphate of potassa (*H. Rose*).

6. *Hydrofluosilicic acid* throws down from solutions of baryta SILICOFLUORIDE OF BARIUM ($Ba\ Fl + Si\ Fl_2$), in form of a colorless, crystalline, quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is perceptibly soluble in hydrochloric and nitric acids. Addition of an equal volume of alcohol hastens the precipitation and makes it so complete that the filtrate remains clear upon addition of sulphuric acid.

7. *Phosphate of soda* produces in neutral or alkaline solutions of baryta a white precipitate of PHOSPHATE OF BARYTA ($2\ Ba\ O, H\ O, P\ O_5$), which is soluble in free acids. Addition of ammonia only slightly increases the quantity of this precipitate; chloride of ammonium dissolves it to a clearly perceptible extent.

8. *Oxalate of ammonia* produces in moderately dilute solutions of baryta a white, pulverulent precipitate of OXALATE OF BARYTA ($Ba\ O, \overline{O} + aq.$), which is soluble in hydrochloric and nitric acids. When recently thrown down, this precipitate dissolves also in oxalic and acetic acids; but the solutions speedily deposit binoxalate of baryta ($Ba\ O, \overline{O} + H\ O, \overline{O} + 2\ aq.$) in the form of a crystalline powder.

9. Salts of baryta in powder, when heated with dilute *spirit of wine*, impart to the flame a YELLOWISH colour, which, however, is not very characteristic.

10. Salts of baryta, particularly chloride of barium, when exposed on a platinum wire to the *inner blowpipe flame*, color the outer flame YELLOWISH-GREEN. With chloride of barium and nitrate and acetate of baryta this reaction is the most distinct, but it is also shown by carbonate and sulphate of baryta. The presence of salts of lime and strontia does not prevent the reaction; addition of chloride of silver considerably heightens its intensity.

§ 95.

b. STRONTIA ($Sr\ O$).

1. Strontia and its hydrate and salts manifest nearly the same general deportment and properties as baryta and its corresponding compounds.—Hydrate of strontia is more difficulty soluble in water than hydrate of baryta.—Chloride of strontium dissolves in absolute alcohol, and deliquesces in moist air. Nitrate of strontia is insoluble in absolute alcohol, and does not deliquesce in the air.

2. The salts of strontia manifest with *ammonia* and *potassa*, and also

with the *alkaline carbonates* and with *phosphate of soda*, nearly the same deportment as the salts of baryta. Carbonate of strontia dissolves somewhat more difficultly in chloride of ammonium than is the case with carbonate of baryta.

3. *Sulphuric acid* and *sulphates* precipitate from solutions of strontia SULPHATE OF STRONTIA ($Sr\,O, S\,O_3$), in form of a white powder, which is insoluble in dilute acids and alkalies. Application of heat greatly promotes the precipitation. Sulphate of strontia is far more soluble in water than sulphate of baryta; owing to this readier solubility, the precipitated sulphate of strontia separates from rather dilute solutions in general only after the lapse of some time; and this is invariably the case (even in concentrated solutions) if *solution of sulphate of lime* is used as precipitant. In boiling hydrochloric acid sulphate of strontia dissolves perceptibly, a solution of the kind showing, after dilution with water, a distinct turbidity upon the addition of a drop of solution of chloride of barium. Sulphate of strontia is readily and completely decomposed by fusion with carbonates of the alkalies, and by boiling with their solutions; it is decomposed also when long digested in the cold with solution of carbonate of ammonia, or boiled with a solution of 1 part of carbonate of potassa and 3 parts of sulphate of potassa (difference from sulphate of baryta).

4. *Hydrofluosilicic acid* fails to produce a precipitate even in concentrated solutions of strontia; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

5. *Oxalate of ammonia* precipitates even from rather dilute solutions, OXALATE OF STRONTIA ($2\,Sr\,O, \overline{O} + 5\,aq.$), in form of a white powder, which dissolves readily in hydrochloric and nitric acid, and perceptibly in salts of ammonia, but is only sparingly soluble in oxalic and acetic acid.

6. If salts of strontia soluble in water or alcohol are heated with dilute spirit of wine, and then kindled, the flame appears of an intense CARMINE color, more particularly upon stirring the alcoholic mixture.

7. *Chloride of strontium* when exposed on platinum wire to the *inner blowpipe flame*, imparts an intense RED color to the outer flame. With carbonate and sulphate of strontia the coloration is less intense; addition of chloride of silver, however, makes the reaction with these two salts also lasting and distinct. Presence of baryta prevents this reaction of strontia.

§ 96.

c. LIME ($Ca\,O$).

1. Lime and its hydrate and salts present, in their general deportment and properties, a great similarity to baryta and strontia and their corresponding compounds. Hydrate of lime is far more difficultly soluble in water than the hydrates of baryta and strontia; it dissolves, besides, more sparingly in hot than in cold water. Hydrate of lime loses its water upon ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol, and deliquesce in the air.

2. *Ammonia, potassa, alkaline carbonates,* and *phosphate of soda,* present nearly the same deportment with salts of lime as with salts of

baryta. Recently precipitated carbonate of lime (CaO, CO_2) is bulky and amorphous—after a time, and immediately upon application of heat, it falls down and assumes a crystalline form. When recently precipitated, it dissolves pretty readily in solution of chloride of ammonium; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in form of crystals.

3. *Sulphuric acid* and *sulphate of soda* produce immediately in very concentrated solutions of lime white precipitates of SULPHATE OF LIME (CaO, SO_3, HO + aq.), which redissolve completely in a large proportion of water, and are still far more soluble in acids. In less concentrated solutions the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in dilute solutions. Solution of sulphate of lime of course cannot produce a precipitate in salts of lime; but even a cold saturated solution of sulphate of potassa, mixed with 3 parts of water, produces a precipitate only after standing from twelve to twenty-four hours. In solutions of lime which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will immediately form upon addition of alcohol. When fused with carbonates of the alkalies, or boiled or digested with their solutions, sulphate of lime comports itself the same as sulphate of strontia.

4. *Hydrofluosilicic acid* does not precipitate salts of lime.

5. *Oxalate of ammonia* produces even in very dilute solutions of lime a white pulverulent precipitate of OXALATE OF LIME. The composition of this precipitate, when thrown down hot or from concentrated solutions, is CaO, C_2O_3 + aq.; whilst when thrown down cold from dilute solutions, it consists of a mixture of CaO, C_2O_3 + aq. with CaO, C_2O_3 + 3 aq. In very dilute solutions the precipitate forms only after some time. It is readily soluble in hydrochloric and nitric acids, but dissolves to a trifling extent only in acetic and oxalic acids.

6. Soluble salts of lime, when heated with dilute *spirit of wine*, impart to the flame of the latter a YELLOWISH-RED color, which is often confounded with that communicated to the flame of alcohol by salts of strontia.

7. *Chloride of calcium*, when exposed on a platinum wire to the *inner blowpipe flame*, imparts a RED colour to the outer flame. With the other salts of lime this reaction is less intense; with phosphate and borate of lime it fails altogether. Chloride of silver, as a rule, heightens the intensity of the color. Presence of baryta prevents this reaction of lime.

§ 97.

d. MAGNESIA (MgO).

1. Magnesia and its hydrate are white powders of far greater bulk than the other alkaline earths and their hydrates. Magnesia and hydrate of magnesia are nearly insoluble both in cold and hot water. Hydrate of magnesia loses its water upon ignition.

2. Some of the salts of magnesia are soluble in water, others are insoluble in that fluid. The soluble salts of magnesia have a nauseous bitter taste; in the neutral state they do not alter vegetable colors; with the exception of sulphate of magnesia, they undergo decomposition when ignited, and the greater part of them even upon simple evaporation of their solutions. Nearly all the salts of magnesia which are insoluble in water dissolve in hydrochloric acid.

3. *Ammonia* throws down from the solutions of neutral salts of magnesia part of the magnesia as hydrate ($Mg\,O, H\,O$), in form of a white, bulky precipitate. The rest of the magnesia remains in solution as a double salt, viz., in combination with the ammoniacal salt which forms upon the decomposition of the salt of magnesia; these double salts are not decomposed by ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds, that ammonia fails to precipitate them in presence of ammoniacal salts in sufficient proportion, or, what is the same, that ammonia produces no precipitate in solutions of magnesia containing a sufficient quantity of free acid; and that precipitates produced by ammonia in neutral solutions of magnesia are redissolved upon the addition of chloride of ammonium.

4. *Potassa, soda,* and *caustic baryta* throws down from solution of magnesia HYDRATE OF MAGNESIA. The separation of this precipitate is greatly promoted by boiling the mixture. Chloride of ammonium and other similar salts of ammonia redissolve the precipitated hydrate of magnesia if the precipitant has not been added greatly in excess. If the salts of ammonia are added in sufficient quantity to the solution of magnesia before the addition of the precipitant, small quantities of the latter fail altogether to produce a precipitate. However, upon boiling the solution afterwards with an excess of potassa, the precipitate will of course make its appearance, since this process causes the decomposition of the ammoniacal salt, removing thus the agent which retains the hydrate of magnesia in solution.

5. *Carbonate of potassa* and *carbonate of soda* produce in neutral solutions of magnesia a white precipitate of BASIC CARBONATE OF MAGNESIA $3\,(Mg\,O, C\,O_2, + aq.) + Mg\,O, H\,O$. One fourth of the carbonic acid of the decomposed alkaline carbonate is liberated in the process, and combines with a portion of the carbonate of magnesia to bicarbonate, which remains in solution. This carbonic acid escapes upon ebullition; application of heat therefore promotes the separation and increases the quantity of the precipitate. Chloride of ammonium and other similar salts of ammonia prevent this precipitation also, and redissolve the precipitates already formed.

6. *Carbonate of ammonia* does not precipitate solutions of magnesia in the cold (at least never immediately, nor even after a short time); upon boiling, it precipitates them only incompletely. Addition of chloride of ammonium and other similar salts of ammonia, in sufficient quantity, entirely prevents the formation of a precipitate.

7. *Phosphate of soda* precipitates from solutions of magnesia, if they are not too dilute, PHOSPHATE OF MAGNESIA ($2\,Mg\,O, H\,O, P\,O_5$) as a white powder. The separation of the precipitate is greatly promoted by ebullition. But if the addition of the precipitant is preceded by that of chloride of ammonium and ammonia, a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\,Mg\,O, N\,H_4\,O, P\,O_5 + 12\,aq.$) will separate, even from very dilute solutions of magnesia; its separation may be greatly promoted and accelerated by vigorous stirring with a glass rod: even should the solution be so extremely dilute as to forbid the formation of a precipitate, yet the lines of direction in which the glass rod has moved along the side of the vessel will after the lapse of some time appear distinctly as white streaks. Water and solutions of salts of ammonia dissolve the precipitate but very slightly; but it is

readily soluble in acids, even in acetic acid. In water containing ammonia it may be considered insoluble.

8. *Oxalate of ammonia* produces no precipitate in highly dilute solutions of magnesia; in less dilute solutions no precipitate is formed at first, but after some time crystalline crusts of various oxalates of ammonia and magnesia make their appearance. In highly concentrated solutions oxalate of ammonia very speedily produces precipitates of oxalate of magnesia ($Mg\,O, \overline{O} + 2\,aq.$), which contain small quantities of the above-named double salts. Chloride of ammonium, especially in presence of free ammonia, interferes with the formation of these precipitates; but, as a rule, it does not absolutely prevent it.

9. *Sulphuric acid* and *hydrofluosilicic acid* do not precipitate salts of magnesia.

10. If magnesia, or a salt of magnesia, is moistened with water, heated to redness on a charcoal support, then moistened with 1 drop of solution of *nitrate of protoxide* of cobalt, and again heated at first to gentle redness, ultimately to intense redness, in the oxidation flame, a pinkish mass is obtained, the color of which becomes distinctly apparent only upon cooling, but is never very intense. Alkalies, alkaline earths, and heavy metallic oxides prevent the reaction.

§ 98.

Recapitulation and remarks.—The difficult solubility of the hydrate of magnesia, the ready solubility of the sulphate, and the disposition of salts of magnesia to form double salts with ammoniacal compounds, are the three principal points in which magnesia differs from the other alkaline earths. To detect magnesia we always first remove the baryta, strontia, and lime, if these bodies happen to be present. In cases requiring no very high degree of accuracy, and where the quantity of salts of ammonia present in the solution is inconsiderable, this removal may be effected by means of carbonate of ammonia and ammonia; but the separation is never perfect, owing to the solvent action which salts of ammonia exercise more especially upon carbonate of baryta and lime; indeed, minute traces of baryta and lime can rarely be precipitated in this manner. Baryta is separated the most completely by sulphuric acid or a sulphate; lime, by oxalate of ammonia in presence of ammonia and some chloride of ammonium; strontia, in the same manner as lime, or by ammonia and carbonate of ammonia in presence of chloride of ammonium. After the removal of the other alkaline earths, the *magnesia* may be readily detected in the filtrate by phosphate of soda in conjunction with ammonia. The detection of *baryta* is an easy task under any circumstances; since the precipitate of sulphate of baryta which separates from baryta solutions immediately upon the addition of sulphate of lime, and the reaction of baryta with hydrofluosilicic are indubitable proofs of the presence of this earth. *Strontia* may likewise be readily detected by its deportment with solution of sulphate of lime, provided of course no baryta be present. If baryta is present, the detection of the strontia may be effected by converting the two earths into dry chlorides, and digesting the latter with absolute alcohol; the greater part of the chloride of barium is left undissolved, whilst the chloride of strontium dissolves; if the alcohol is now heated, and then ignited, the carmine tint of the flame will indicate the presence of strontia. However, the results obtained in this way can only be considered satisfactory if the

quantity of the strontia is not too minute, and if there is not much lime present; since in the latter case the yellowish-red flame of the lime will mask the carmine flame of the strontia. In cases of this kind strontia is detected best by the following process. Mix the solution containing baryta, strontia, and lime with hydrofluosilicic acid and a volume of alcohol equal to that of the fluid present; let the mixture stand several hours; filter off the silicofluoride of barium, and mix the filtrate with sulphuric acid; filter the precipitate formed, wash, and convert the sulphates into carbonates by boiling with solution of carbonate of soda; wash the carbonates, dissolve them in a small quantity of hydrochloric acid, and test the solution for strontia with solution of sulphate of lime. The precipitate of sulphate of strontia thus obtained may then be tested before the blowpipe, with addition of chloride of silver. For the detection of *lime* we invariably select oxalate of ammonia. Before applying this test, however, baryta and strontia must be removed, as they are equally precipitated by it. This removal is effected best by adding to the solution sulphate of potassa in excess, and boiling the mixture for some time. If there is much lime present, a portion of the latter earth precipitates with the baryta and strontia; this is, however, a matter of indifference, since there remains always a sufficient amount of lime in solution to permit the positive and indubitable detection of this substance in the filtrate by oxalate of ammonia; to prevent precipitation of traces of oxalate of strontia, the filtrate must be diluted with $\frac{1}{2}$ volume of water. The best way of effecting the detection of the alkaline earths, when in the form of phosphates, is to decompose these latter by means of sesquichloride of iron with the addition of acetate of soda (§ 143). The oxalates of the alkaline earths are converted into carbonates by ignition, preparatory to the detection of the individual earths which they contain. Sulphate of baryta and sulphate of strontia are fused with alkaline carbonates, to effect the detection of the baryta and strontia (compare § 141). To separate sulphate of baryta from sulphate of strontia and sulphate of lime, digest the finely triturated substance with solution of carbonate of ammonia for twelve hours in the cold, or boil it ten minutes with a solution of 3 parts of sulphate and 1 part of carbonate of potassa; sulphate of strontia and sulphate of lime are decomposed in both cases, whilst sulphate of baryta remains unaltered. Filter, wash thoroughly with hot water, and test the washed residue with dilute hydrochloric acid, which will dissolve the carbonate of strontia and carbonate of lime formed, leaving the sulphate of baryta undissolved (*H. Rose*).

§ 99.

THIRD GROUP.

Alumina, Sesquioxide of Chromium.

Properties of the group.—Alumina and sesquioxide of chromium are insoluble in water, both in the pure state and as hydrates. They form no neutral salts with carbonic acid. Their sulphides cannot be produced in the humid way. Hydrosulphuric acid therefore fails to precipitate solutions of alumina and sesquioxide of chromium; sulphide of ammonium precipitates the hydrated oxides from these solutions. This deportment with sulphide of ammonium distinguishes the oxides of the third from those of the two preceding groups.

Special Reactions.

§ 100.

a. ALUMINA ($Al_2 O_3$).

1. Alumina is non-volatile and colorless; the hydrate is also colorless. Alumina dissolves in acids (particularly when dilute) slowly and with very great difficulty; in fusing bisulphate of potassa it dissolves readily to a mass soluble in water. The hydrate in an amorphous state, and recently precipitated, is readily soluble in acids; but after being left some time in the fluid from which it was precipitated, its solubility decreases, and in the crystallized state it dissolves with very great difficulty in acids. After previous ignition with alkalies, which leads to the formation of aluminates of the alkalies, alumina is readily dissolved by acids.

2. The salts of alumina are colorless, and most of them are non-volatile: some of them are soluble, others insoluble. The soluble salts have a sweetish, astringent taste, redden litmus-paper, and lose their acids upon ignition. The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds of alumina; the compounds of alumina which are insoluble in hydrochloric acid are decomposed and made soluble by ignition with carbonate of soda and potassa, or bisulphate of potassa.

3. *Potassa* and *soda* throw down from solutions of alumina a bulky precipitate of HYDRATE OF ALUMINA ($Al_2 O_3$, 3 H O), which contains alkali, and generally also an admixture of basic salt; this precipitate redissolves readily and completely in an excess of the precipitant, but from this solution it is reprecipitated by addition of chloride of ammonium, even in the cold, but more completely upon application of heat (compare § 51). The presence of salts of ammonia does not prevent the precipitation by potassa or soda.

4. *Ammonia* also produces in solutions of alumina a precipitate of HYDRATE OF ALUMINA, containing ammonia and an admixture of basic salt; this precipitate also redissolves in a very considerable excess of the precipitant, but with difficulty only, which is the greater the larger the quantity of salts of ammonia contained in the solution. It is this deportment which accounts for the complete precipitation of hydrate of alumina from solution in potassa, by an excess of chloride of ammonium.

5. If the solution of a salt of alumina is digested with finely pulverized carbonate of baryta, the greater part of the acid of the alumina salt combines with the baryta, the liberated carbonic acid escapes, and the alumina precipitates completely as HYDRATE mixed with BASIC SALT OF ALUMINA; even digestion in the cold suffices to produce this reaction.

6. If alumina or one of its compounds is ignited upon charcoal before the blowpipe, and afterwards moistened with a solution of *nitrate of protoxide of cobalt*, and then again strongly ignited, an unfused mass of a deep SKY-BLUE color is produced, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candlelight it appears violet. This reaction is decisive only in the case of infusible or difficultly fusible compounds of alumina pretty free from other oxides, as solution of cobalt imparts a blue tint to readily fusible salts, even though no alumina be present.

§ 101.

b. SESQUIOXIDE OF CHROMIUM (Cr_2O_3).

1. Sesquioxide of chromium is a green, its hydrate a bluish gray-green powder. The hydrate dissolves readily in acids; the non-ignited sesquioxide dissolves more difficultly, and the ignited sesquioxide is almost altogether insoluble.

2. The salts of sesquioxide of chromium have a green or violet color. Many of them are soluble in water. Most of them dissolve in hydrochloric acid. The solutions usually exhibit a fine green color. Many double salts of sesquioxide of chromium, *e.g.*, sulphate of sesquioxide of chromium and potassa (chrome alum), have a deep violet color, and give with cold water bluish-violet solutions which, however, acquire a green tint when even moderately heated. The salts of sesquioxide of chromium with volatile acids are decomposed upon ignition, the acids being expelled. The salts of sesquioxide of chromium which are soluble in water redden litmus.

3. *Potassa and soda* produce in solutions of salts of sesquioxide of chromium a bluish-green precipitate of HYDRATE OF SESQUIOXIDE OF CHROMIUM, which dissolves readily and completely in an excess of the precipitant, imparting to the fluid generally an emerald-green tint, but in cases where the solution originally precipitated was bluish-violet, a violet color. Upon *long-continued* ebullition of this solution, the whole of the hydrated sesquioxide separates again, and the supernatant fluid appears perfectly colorless. The same reprecipitation takes place if chloride of ammonium is added to the alkaline solution, and the mixture heated. If the alkaline solution of sesquioxide of chromium is gently heated with binoxide of lead, the sesquioxide of chromium is converted into chromic acid, and the alkaline fluid now holds chromate of lead in solution; upon supersaturation with acetic acid, chromate of lead separates in form of a yellow precipitate.

4. *Ammonia* also produces in solutions of salts of sesquioxide of chromium a precipitate of HYDRATE OF SESQUIOXIDE OF CHROMIUM: this precipitate contains more or less water, according as the ammonia has been added gradually or suddenly, and appears, therefore, sometimes grayish-green, sometimes grayish-blue. A small portion of it redissolves in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red tint; but if, after the addition of ammonia in excess, heat is applied to the mixture, the precipitation is complete.

5. *Carbonate of baryta* precipitates from solutions of sesquioxide of chromium the whole of the sesquioxide as a GREENISH HYDRATE mixed with BASIC SALT. The precipitation takes place in the cold, but is complete only after long-continued digestion.

6. The fusion of sesquioxide of chromium or of any of its compounds with *nitrate of soda and some carbonate of soda* gives rise to the formation of yellow CHROMATE OF SODA, part of the oxygen of the nitric acid separating from the nitrate of soda, and converting the sesquioxide of chromium into chromic acid, which then combines with the soda. For the reactions of chromic acid, see § 138.

7. *Phosphate of soda and ammonia* dissolves sesquioxide of chromium and its salts, both in the *oxidizing* and *reducing* flame of the blowpipe, to clear beads of a faint YELLOWISH-GREEN tint, which upon cooling

changes to EMERALD-GREEN. The sesquioxide of chromium and its salts show a similar deportment with *biborate of soda.*

§ 102.

Recapitulation and remarks.—The solubility of hydrate of alumina in solutions of potassa and soda, and its reprecipitation from the alkaline solutions by chloride of ammonium, afford a safe means of detecting alumina only in the absence of sesquioxide of chromium. If the latter is present therefore, which is seen either from the color of the solution, or by the reaction with phosphate of soda and ammonia, it must be removed before we can proceed to test for alumina. The separation of sesquioxide of chromium from alumina is effected the most completely by fusing 1 part of the mixed oxides together with 2 parts of carbonate and 2 parts of nitrate of soda, which may be done in a platinum crucible. The yellow mass obtained is boiled with water; by this process the whole of the chromium is dissolved as chromate of soda, and part of the alumina as aluminate of soda, the rest of the alumina remaining undissolved. If the solution is acidified with nitric acid, it acquires a reddish tint; if ammonia is then added to feebly alkaline reaction, the dissolved portion of the alumina separates.

The precipitation of sesquioxide of chromium, effected by boiling its solution in solution of potassa or soda, is also sufficiently reliable if the ebullition is continued a sufficient length of time; still it is often liable to mislead in cases where only little sesquioxide of chromium is present, or where the solution contains organic matter, even though in small proportion only. The deportment of a solution of sesquioxide of chromium with solution of potassa or soda is completely changed by the presence of certain other metallic oxides, especially oxide of zinc, oxide of lead, sesquioxide of iron; in presence of these oxides, and according to the greater or less relative proportion in which they happen to be present, sesquioxide of chromium does not dissolve, or dissolves only incompletely in an excess of solution of potassa. This circumstance should never be lost sight of in the analysis of compounds containing sesquioxide of chromium. Lastly, it must be borne in mind, also, that alkalies produce no precipitates in the solutions of alumina if non-volatile organic substances are present, such as sugar, tartaric acid, &c.; whilst the precipitation of sesquioxide of chromium is less seriously interfered with by the presence of such bodies.

§ 103.

SUPPLEMENT TO THE THIRD GROUP.

TITANIC ACID (TiO_2).

From among the other oxides enumerated in § 86 as belonging to the third group, we have selected titanic acid as deserving of special notice, since this substance is met with more frequently than the others in analytical investigations, more especially also in the analysis of the slag adhering to the bottom of blast furnaces in which iron ore is reduced, which slag is often found to contain small copper-coloured cubes, consisting of a combination of cyanide of titanium with nitride of titanium (*Wöhler*).

Titanium burns in the air with considerable brilliancy to titanic acid

(TiO_2). Besides the acid, another oxide of titanium is known, the sesquioxide (Ti_2O_3). According to the different mode of its preparation, titanic acid appears sometimes as a white powder, which, when heated, transiently acquires a yellow tint, sometimes in the form of small lumps of a reddish-brown color. It is infusible, and insoluble in water and acid, with the exception of concentrated sulphuric acid. With bisulphate of potassa it fuses into a mass, which dissolves in a large proportion of cold water to a clear fluid. Fusion of titanic acid with carbonate of soda gives rise to the formation of titanate of soda, which is by addition of water converted into soda and bititanate of soda; the latter salt is insoluble in water, but soluble in hydrochloric acid. The hydrate of titanic acid is white; it dissolves, both in the moist state and when dried without the aid of heat, in dilute acids, especially hydrochloric and sulphuric acids. Solutions of titanic acid in hydrochloric or sulphuric acid, but more especially the latter, when subjected in a highly dilute state to long-continued ebullition, deposit titanic acid as a white powder, insoluble in dilute acids. The precipitate thus formed in hydrochloric acid cannot be separated by filtration, unless an acid or chloride of ammonium is added, as it will pass through the filter with the washing water. Solution of potassa throws down from solutions of titanic acid in hydrochloric or sulphuric acid, hydrate of titanic acid in form of a bulky, white precipitate, which is insoluble in an excess of the precipitant; ammonia, sulphide of ammonium, carbonates of the alkalies, and carbonate of baryta act in the same way. The precipitate, if thrown down without application of heat, and washed with cold water, is soluble in hydrochloric acid and dilute sulphuric acid; presence of tartaric acid prevents its formation. Ferrocyanide of potassium produces in acid solutions of titanic acid a dark brown precipitate; infusion of galls a brownish precipitate, which speedily turns orange-red. Metallic zinc produces, in consequence of the ensuing reduction of titanic acid to sesquioxide of titanium, at first a blue coloration of the solution, afterwards a blue precipitate of hydrate of sesquioxide of titanium. Phosphate of soda and ammonia readily dissolves titanic acid in the outer flame of the blowpipe to a clear bead of a yellowish color whilst hot, but colorless when cold. If this bead is exposed to the reducing flame, it acquires a yellow tint, which turns to red when the bead is half cold, and to violet when quite cold.

§ 104.

FOURTH GROUP.

Oxide of Zinc, Protoxide of Manganese, Protoxide of Nickel, Protoxide of Cobalt, Protoxide of Iron, Sesquioxide of Iron.

Properties of the group.—The solutions of the oxides of the fourth group, when containing a stronger free acid, are not precipitated by hydrosulphuric acid; neutral solutions also are not, or only very incompletely, precipitated by that reagent; but alkaline solutions are completely precipitated by hydrosulphuric acid; and other solutions also if a sulphide of an alkali metal is used as the precipitant, instead of hydrosulphuric acid. The precipitated metallic sulphides corresponding

to the respective oxides are insoluble in water; some of them are readily soluble in dilute acids; others (sulphide of nickel and sulphide of cobalt) dissolve only with very great difficulty in these menstrua. Some of them are insoluble in sulphides of the alkali metals; others are sparingly soluble in them, under certain circumstances.

Special Reactions.

§ 105.

a. OXIDE OF ZINC ($Zn\,O$).

1. Metallic zinc is bluish-white and very bright; when exposed to the air, a thin coating of basic carbonate of zinc forms on its surface. It is of medium hardness, ductile at a temperature of between 212° and 302° Fah., and under ordinary circumstances more or less brittle; it fuses readily on charcoal before the blowpipe, boils afterwards, and burns with a bluish-green flame, giving off white fumes, and coating the charcoal support with oxide. Zinc dissolves in hydrochloric and sulphuric acids, with evolution of hydrogen gas; in dilute nitric acid, with evolution of nitrous oxide; in more concentrated nitric acid, with evolution of nitric oxide.

2. The oxide of zinc and its hydrate are white powders, which dissolve readily in hydrochloric, nitric, and sulphuric acids. The oxide of zinc acquires a lemon-yellow tint when heated, but it reassumes its original white color upon cooling. When ignited before the blowpipe, it shines with considerable brilliancy.

3. The compounds of oxide of zinc are colorless; part of them are soluble in water, the rest in acids. The neutral salts of zinc which are soluble in water redden litmus-paper, and are readily decomposed by heat, with the exception of sulphate of zinc, which can bear a dull red heat, without undergoing decomposition. Chloride of zinc is volatile at a red heat.

4. *Hydrosulphuric acid* precipitates from neutral solutions of salts of zinc a portion of the metal as white hydrated SULPHIDE of ZINC ($Zn\,S$). In acid solutions this reagent fails altogether to produce a precipitate if the free acid present is one of the stronger acids; but from a solution of oxide of zinc in acetic acid, it throws down the whole of the zinc, even if the acid is present in excess.

5. *Sulphide of ammonium* throws down from *neutral*, and *hydrosulphuric acid* from *alkaline* solutions of salts of zinc, the whole of the metal as hydrated SULPHIDE OF ZINC, in form of a white precipitate. This precipitate is not redissolved by an excess of sulphide of ammonium, nor by potassa or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid.

6. *Potassa and soda* throw down from solutions of salts of zinc HYDRATED OXIDE OF ZINC ($Zn\,O, H\,O$), in form of a white, gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant. Upon boiling these alkaline solutions they remain, if concentrated, unaltered; but from dilute solutions nearly the whole of the oxide of zinc separates as a white precipitate. Chloride of ammonium does not precipitate alkaline solutions of oxide of zinc. If a solution of oxide of zinc in solution of potassa or soda is mixed with a solution of sesquioxide of chromium also in solution of potassa or soda,

a green precipitate is formed, consisting of a compound of sesquioxide of chromium with oxide of zinc ($Zn\,O,\ Cr_2\,O_3$). A solution of caustic soda or potassa therefore can never contain both oxides together in solution (*Chancel*).

7. *Ammonia* also produces in solutions of oxide of zinc, if they do not contain a large excess of free acid, a precipitate of HYDRATED OXIDE OF ZINC, which readily dissolves in an excess of the precipitant. The concentrated solution turns turbid when mixed with water. On boiling the concentrated solution, part of the oxide of zinc separates immediately; on boiling the dilute solution, all the oxide of zinc precipitates.

8. *Carbonate of soda* produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC ($3\,[Zn\,O,\ H\,O] + 2\,[Zn\,O,\ C\,O_2] + 4$ aq.), which is insoluble in an excess of the precipitant. Presence of salts of ammonia in great excess prevents the formation of this precipitate.

9. *Carbonate of ammonia* also produces in solutions of salts of zinc the same precipitate of BASIC CARBONATE OF ZINC as carbonate of soda; but this precipitate redissolves upon further addition of the precipitant. On boiling the dilute solution, oxide of zinc precipitates.

10. *Carbonate of baryta* fails to precipitate solutions of oxide of zinc in the cold.

11. If a mixture of oxide of zinc, or one of its salts, with *carbonate of soda* is exposed to the *reducing flame* of the blowpipe, the charcoal support becomes covered with a slight coating of OXIDE OF ZINC, which presents a yellow color whilst hot, and turns white upon cooling. This coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and being reoxidized in passing through the outer flame.

12. If oxide of zinc or one of the salts of zinc is moistened with solution of *nitrate of protoxide of cobalt*, and then heated before the blowpipe, an unfused mass is obtained, of a beautiful GREEN color: this mass is a compound of oxide of zinc with protoxide of cobalt. If therefore in the experiment described in 11 the charcoal is moistened, around the little cavity, with solution of nitrate of protoxide of cobalt, the coating appears *green* when *cold*.

§ 106.

b. PROTOXIDE OF MANGANESE ($Mn\,O$).

1. Metallic manganese has a whitish-gray color and but little lustre; it is brittle, and fuses with very great difficulty; it oxidizes slowly in cold water, rapidly in boiling water, and dissolves readily in acids. The solutions contain protoxide.

2. Protoxide of manganese is grayish-green; the hydrated protoxide is white. Both the protoxide and its hydrate absorb oxygen from the air, and are converted into the brown sesquioxide. They are readily soluble in hydrochloric, nitric, and sulphuric acids.

3. The salts of protoxide of manganese are colorless or pale red; part of them are soluble in water, the rest in acids. The salts soluble in water are readily decomposed by a red heat, with the exception of the sulphate. The solutions do not alter vegetable colors.

4. *Hydrosulphuric acid* does not precipitate acid solutions of salts of protoxide of manganese; neutral solutions also it fails to precipitate, or precipitates them only very imperfectly.

5. *Sulphide of ammonium* throws down from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of protoxide of manganese, the whole of the metal as hydrated SULPHIDE OF MANGANESE (Mn S), in form of a light flesh-colored* precipitate, which acquires a dark-brown color in the air; this precipitate is insoluble in yellow sulphide of ammonium and in alkalies, soluble to a very trifling extent in colorless sulphide of ammonium, but readily soluble in hydrochloric and nitric acids. From very dilute solutions the precipitate separates only after standing some time in a warm place.

6. *Potassa, soda,* and *ammonia* produce whitish precipitates of HYDRATE OF PROTOXIDE OF MANGANESE (Mn O, H O), which upon exposure to the air speedily acquire a brownish and finally a deep blackish-brown color, owing to the conversion of the hydrated protoxide into hydrated sesquioxide, by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate; but presence of chloride of ammonium prevents the precipitation by ammonia altogether, and that by potassa partly. Of *already formed* precipitates solution of chloride of ammonium redissolves only those parts which have not yet undergone peroxidation. The solution of the hydrated protoxide of manganese in chloride of ammonium is owing to the disposition of the salts of protoxide of manganese to form double salts with salts of ammonia. The ammoniacal solutions of the double salts turn brown in the air, and deposit dark-brown hydrate of, sesquioxide of manganese (*Otto*).

7. If a few drops of a fluid containing protoxide of manganese, and free from chlorine, are sprinkled on binoxide of lead, or red-lead, nitric acid free from chlorine added, the mixture boiled and allowed to settle, the fluid is of a purple red color from the formation of permanganic acid.

8. *Carbonate of baryta* does not precipitate protoxide of manganese from its solutions, upon digestion in the cold.

9. If any compound of manganese, in a state of minute division, is fused with *carbonate of soda* on a platinum wire in the *outer* flame of the blowpipe, MANGANATE OF SODA (Na O, Mn O_3) is formed, which makes the fused mass appear GREEN while hot, and of a BLUISH-GREEN tint after cooling, the bead at the same time becoming turbid. This reaction enables us to detect the smallest quantities of manganese. The delicacy of the test may be still further increased by the addition of a minute quantity of nitrate of potassa to the carbonate of soda.

10. *Borax* and *phosphate of soda and ammonia* dissolve manganese compounds in the *outer* flame of the blowpipe to clear VIOLET-RED beads, which upon cooling acquire an AMETHYST-RED tint: they lose their color in the *inner* flame, owing to a reduction of the sesquioxide to protoxide. The bead which borax forms with manganese compounds appears black when containing a considerable portion of sesquioxide of manganese, but that formed by phosphate of soda and ammonia never loses its transparency. But the latter loses its color in the inner flame of the blowpipe far more readily than the former.

§ 107.

c. PROTOXIDE OF NICKEL (Ni O).

1. Metallic nickel in the fused state is silvery white, inclining to gray;

* If the quantity of the precipitate is only trifling, the color appears yellowish-white.

it is bright, hard, malleable, ductile, difficultly fusible; it does not oxidize in the air at common temperatures, but it oxidizes slowly upon ignition; it is attracted by the magnet, and may itself become magnetic. It slowly dissolves in hydrochloric acid and dilute sulphuric acid upon the application of heat, the solution being attended with evolution of hydrogen gas. It dissolves readily in nitric acid.

2. Protoxide of nickel is a gray, its hydrate a green powder. Both the protoxide and its hydrate are unalterable in the air, and readily soluble in hydrochloric, nitric, and sulphuric acids.

3. Most of the salts of protoxide of nickel are yellow in the anhydrous, green in the hydrated state; their solutions are of a light green color. The soluble neutral salts slightly redden litmus paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* does not precipitate acid solutions of salts of nickel; it fails also to precipitate neutral solutions of salts of nickel with the stronger acids, or it precipitates them only very imperfectly.

5. *Sulphide of ammonium* produces in neutral, and *hydrosulphuric acid* in alkaline solutions of salts of protoxide of nickel, a black precipitate of hydrated SULPHIDE OF NICKEL (Ni S), which is not altogether insoluble in sulphide of ammonium, especially if containing free ammonia; the fluid from which the precipitate has been thrown down exhibits therefore usually a brownish color. Sulphide of nickel dissolves with great difficulty in hydrochloric acid, but readily in nitrohydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce a light green precipitate of HYDRATE OF PROTOXIDE OF NICKEL (Ni O, H O), which is insoluble in an excess of the precipitants, and unalterable in the air. Carbonate of ammonia dissolves this precipitate, when filtered and washed, to a greenish-blue fluid, from which potassa or soda reprecipitates the nickel as an apple-green hydrate of protoxide of nickel.

7. *Ammonia* added in small quantity to solutions of protoxide of nickel produces in them a trifling greenish turbidity; upon further addition of the reagent this redissolves readily to a blue fluid containing a compound of protoxide of nickel and ammonia. Potassa and soda precipitate from this solution hydrate of protoxide of nickel. Solutions containing salts of ammonia or free acid are not rendered turbid by ammonia.

8. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL (Ni Cy), which redissolves readily in an excess of the precipitant as a double cyanide of nickel and potassium (Ni Cy + K Cy); the solution is brownish-yellow. If sulphuric acid or hydrochloric acid is added to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel reprecipitated; the latter substance is very difficultly soluble in an excess of these acids in the cold, but more readily upon boiling.

9. *Carbonate of baryta* does not precipitate protoxide of nickel from its solutions, upon digestion in the cold.

10. *Nitrite of potassa*, used in conjunction with acetic acid, fails to precipitate even concentrated solutions of nickel.

11. *Borax* and *phosphate of soda and ammonia* dissolve compounds of protoxide of nickel in the *outer* flame of the blowpipe to clear beads; the bead produced with borax is violet whilst hot, reddish-brown when cold; the bead produced with the phosphate of soda and ammonia is reddish, inclining to brown whilst hot, but turns yellow or reddish-yellow upon cool-

ing. The bead which phosphate of soda and ammonia forms with salts of protoxide of nickel remains unaltered in the *inner* flame of the blowpipe, but that formed with borax turns gray and turbid from reduced metallic nickel. Upon continued exposure to the blowpipe flame the particles of nickel unite, but without fusing to a grain, and the bead becomes colorless.

§ 108.

d. PROTOXIDE OF COBALT (Co O).

1. Metallic cobalt is reddish-gray, slightly lustrous, pretty hard, slightly malleable, ductile, and difficultly fusible ; it does not oxidize in the air at the common temperature, and oxidizes only slowly at a red heat ; with acids it comports itself like nickel.

2. Protoxide of cobalt is an olive-green, its hydrate a pale red powder. Both dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The salts of protoxide of cobalt, containing water of crystallization, are red, the anhydrous salts mostly blue. The moderately concentrated solutions appear of a light red color, which they retain even though considerably diluted. The soluble neutral salts redden litmus paper slightly, and are decomposed at a red heat ; sulphate of protoxide of cobalt alone can bear a moderate red heat without suffering decomposition. When a solution of chloride of cobalt is evaporated, the light red color changes towards the end of the operation to blue; addition of water restores the red color.

4. *Hydrosulphuric acid* does not precipitate acid solutions of cobalt ; it also fails to precipitate neutral solutions of salts of protoxide of cobalt with the stronger acids, or it precipitates them only very imperfectly.

5. *Sulphide of ammonium* precipitates from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of protoxide of cobalt, the whole of the metal as black hydrated SULPHIDE OF COBALT (Co S). This substance is insoluble in alkalies and sulphide of ammonium, very difficultly soluble in hydrochloric acid, but readily so in nitrohydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce in solutions of cobalt BLUE precipitates of basic salts of cobalt, which turn GREEN upon exposure to the air, owing to the absorption of oxygen ; upon boiling, they are converted into pale red hydrate of protoxide of cobalt, which contains alkali, and generally appears rather discolored from an admixture of sesquioxide formed in the process. These precipitates are insoluble in solutions of potassa and soda ; but neutral carbonate of ammonia dissolves them completely to intensely violet-red fluids, in which a somewhat larger proportion of potassa or soda produces a blue precipitate, the fluid still retaining its violet color.

7. *Ammonia* produces the same precipitate as potassa, but this redissolves in an excess of the ammonia to a reddish-brown fluid, from which solution of potassa or soda throws down part of the cobalt as a blue basic salt. Ammonia fails to precipitate solutions of protoxide of cobalt containing salts of ammonia or free acid.

8. Addition of *cyanide of potassium* to a solution of cobalt gives rise to the formation of a brownish-white precipitate of PROTOCYANIDE OF COBALT (Co Cy), which dissolves readily as a double cyanide of cobalt and potassium in an excess of solution of cyanide of potassium. Acids precipitate from this solution cyanide of cobalt. But if the solution is

boiled with cyanide of potassium in excess, in presence of free hydrocyanic acid (liberated by addition of one or two drops of hydrochloric acid), a double compound of sesquicyanide of cobalt and cyanide of potassium ($K_3, Co_2\,Cy_6 = K_3\,Ckdy$) is formed, in the solution of which acids *produce no precipitate.*

9. *Carbonate of baryta* does not precipitate solution of protoxide of cobalt in the cold.

10. If *nitrite of potassa* is added in not too small proportion to a solution of protoxide of cobalt, then acetic acid to *strongly* acid reaction, and the mixture put in a moderately warm place, all the cobalt separates, from concentrated solutions immediately or very soon, from dilute solutions after some time, as NITRITE OF SESQUIOXIDE OF COBALT AND POTASSA ($Co_2\,O_3, 3\,K\,O, 5\,N\,O_3, 2\,H\,O$), in form of a crystalline precipitate of a beautiful yellow color. The mode in which this precipitate forms may be seen from the following equation: $2\,(Co\,O, S\,O_3) + 6\,(K\,O, N\,O_3) + \bar{A} = K\,O, \bar{A} + 2\,K\,O, S\,O_3 + Co_2\,O_3, 3\,K\,O, 5\,N\,O_3 + N\,O_2$. The precipitate is only sparingly soluble in pure water, and altogether insoluble in saline solutions and in alcohol. When boiled with water, it dissolves, though not copiously, to a red fluid, which remains clear upon cooling, and from which alkalies throw down hydrate of protoxide of cobalt (*Fischer, Aug. Stromeyer*). This excellent reaction enables us to distinguish nickel from cobalt. It is always necessary to concentrate the solution of protoxide of cobalt to a considerable extent before adding the nitrite of potassa.

11. *Borax* dissolves compounds of cobalt both in the *inner* and *outer* flame of the blowpipe, giving clear beads of a magnificent BLUE color, which appear violet by candle-light, and almost black if the cobalt is present in considerable proportion. This test is as delicate as it is characteristic. *Phosphate of soda and ammonia* manifests with salts of cobalt before the blowpipe an analogous but less delicate reaction.

§ 109.

e. PROTOXIDE OF IRON ($Fe\,O$).

1. Metallic iron in the pure state has a light whitish gray color (iron containing carbon is more or less gray); the metal is hard, lustrous, malleable, ductile, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture a coating of rust (hydrate of sesquioxide of iron) forms on its surface; upon ignition in the air, a coating of black protosesquioxide. Hydrochloric acid and dilute sulphuric acid dissolve iron, with evolution of hydrogen gas; if the iron contains carbon, the hydrogen is mixed with carbide of hydrogen. The solutions contain protoxide. Dilute nitric acid dissolves iron in the cold to nitrate of protoxide, with evolution of nitrous oxide; at a high temperature, to nitrate of sesquioxide, with evolution of nitric oxide; if the iron contains carbon, some carbonic acid is also evolved, and there is left undissolved a brown substance resembling humus, which is soluble in alkalies.

2. Protoxide of iron is a black powder; its hydrate is a white powder, which in the moist state absorbs oxygen and speedily acquires a grayish-green, and ultimately a brownish-red color. Both the protoxide and its hydrate are readily dissolved by hydrochloric, sulphuric, and nitric acids.

3. The salts of protoxide of iron have in the anhydrous state a white, in the hydrated state a greenish color; their solutions appear colored only when concentrated. Exposed to the air, they absorb oxygen and are converted into salts of the protosesquioxide. The soluble neutral salts redden litmus paper, and are decomposed at a red heat.

4. Acid solutions of salts of protoxide of iron are not precipitated by *hydrosulphuric acid;* neutral solutions of salts of protoxide of iron with weak acids are precipitated by this reagent at the most but very incompletely; the precipitates are of a black color.

5. *Sulphide of ammonium* precipitates from neutral, and hydrosulphuric acid from alkaline solutions of salts of protoxide of iron, the whole of the metal as black hydrated PROTOSULPHIDE OF IRON (Fe S), which is insoluble in alkalies and sulphides of the alkali metals, but dissolves readily in hydrochloric and nitric acids: this black precipitate turns reddish-brown in the air by oxidation. To highly dilute solutions of protoxide of iron, addition of sulphide of ammonium imparts a green color, and it is only after some time that the protosulphide of iron separates as a black precipitate.

6. *Potassa* and *ammonia* produce a precipitate of HYDRATE OF PROTOXIDE OF IRON (Fe O, H O), which in the first moment looks almost white, but acquires after a very short time a dirty green, and ultimately a reddish-brown color, owing to absorption of oxygen from the air. Presence of salts of ammonia prevents the precipitation by potassa partly, and that by ammonia altogether. If alkaline solutions of protoxide of iron thus obtained by the agency of salts of ammonia are exposed to the air, hydrate of sesquioxide of iron precipitates.

7. *Ferrocyanide of potassium* produces in solutions of protoxide of iron a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON (K, Fe_2, Cfy_2), which, by absorption of oxygen from the air, speedily acquires a blue color. Nitric acid or chlorine converts it immediately into Prussian blue, $3 (K, Fe_2, Cfy_2) + 4 Cl = 3 K Cl + Fe Cl + 2 (Fe_4 Cfy_3)$.

8. *Ferricyanide of potassium* produces a magnificently blue precipitate of FERRICYANIDE OF IRON (Fe_3 Cfdy). This precipitate does not differ in color from Prussian ~~blue. It is~~ insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions of salts of protoxide of iron the reagent produces simply a deep blue-green coloration.

9. *Sulphocyanide of potassium* does not alter solutions of protoxide of iron free from sesquioxide.

10. *Carbonate of baryta* does not precipitate solutions of protoxide of iron in the cold.

11. *Borax* dissolves salts of protoxide of iron in the *oxidizing* flame, giving beads varying in color from YELLOW to DARK RED; when cold, the beads vary from colorless to dark yellow. In the *inner* flame the beads change to bottle-green, owing to the reduction of the newly-formed sesquioxide to protosesquioxide. *Phosphate of soda and ammonia* manifests a similar deportment with the salts of protoxide of iron; the beads produced with this reagent lose their color upon cooling still more completely than is the case with those produced with borax; the signs of the ensuing reduction in the reducing flame are also less marked.

§ 110.

f. Sesquioxide of Iron ($Fe_2 O_3$).

1. The native crystallized sesquioxide of iron is steel-gray; the native as well as the artificially prepared sesquioxide of iron gives upon trituration a brownish-red powder; the color of hydrate of sesquioxide of iron is more inclined to reddish-brown. Both the sesquioxide and its hydrate dissolve in hydrochloric, nitric, and sulphuric acids; the hydrate dissolves readily in these acids, but the anhydrous sesquioxide dissolves with greater difficulty, and completely only after long exposure to heat.

2. The neutral anhydrous salts of sesquioxide of iron are nearly white; the basic salts are yellow or reddish-brown. The color of the solution is brownish-yellow, and becomes reddish-yellow upon the application of heat. The soluble neutral salts redden litmus paper, and are decomposed by heat.

3. *Hydrosulphuric acid* produces in neutral and acid solutions of salts of sesquioxide of iron a milky white turbidity, proceeding from separated SULPHUR. This reaction is caused by a mutual decomposition of the sesquioxide of iron and the hydrosulphuric acid, in which the former is deprived of one-third of its oxygen, and thus reduced to the state of protoxide; the oxygen forms water with the hydrogen of the hydrosulphuric acid, and the liberated sulphur separates. Solution of hydrosulphuric acid, rapidly added to neutral solutions, imparts to the fluid a transitory blackening. In solution of neutral acetate of sesquioxide of iron it produces a permanent precipitate of sulphide of iron.

4. *Sulphide of ammonium* precipitates from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of sesquioxide of iron, the whole of the metal as black hydrated PROTOSULPHIDE OF IRON (Fe S). This precipitation is preceded by the reduction of the sesquioxide to protoxide. In very dilute solutions the reagent produces only a blackish-green coloration. The minutely divided protosulphide of iron subsides in such cases only after long standing. Protosulphide of iron, as already stated (§ 109, 5), is insoluble in alkalies and alkaline sulphides, but dissolves readily in hydrochloric and nitric acids.

5. *Potassa* and *ammonia* produce bulky reddish-brown precipitates of HYDRATE OF SESQUIOXIDE OF IRON ($F_2 O_3$, H O), which are insoluble in an excess of the precipitant as well as in salts of ammonia. In presence of sesquioxide of chromium, an excess of solution of potassa or ammonia will dissolve part of the sesquioxide of iron along with the sesquioxide of chromium. Generally, however, a portion of both oxides remains undissolved; and, moreover, the dissolved oxides speedily separate again from the solution.

6. *Ferrocyanide of potassium* produces even in highly dilute solutions a magnificently blue precipitate of FERROCYANIDE OF IRON, or Prussian blue ($Fe_4 Cfy_3$), which is insoluble in hydrochloric acid, but is decomposed by potassa, with separation of hydrate of sesquioxide of iron.

7. *Ferricyanide of potassium* deepens the color of solutions of salts of sesquioxide of iron to reddish-brown; but it fails to produce a precipitate.

8. *Sulphocyanide of potassium* imparts to neutral or slightly acid solutions of salts of sesquioxide of iron a most intense blood-red color, arising from the formation of a soluble SULPHOCYANIDE OF IRON. Addition of acetate of soda destroys this color, hydrochloric acid restores it

again. This test is the most delicate of all; it will indicate the presence of sesquioxide of iron even in fluids which are so highly dilute that every other reagent fails to produce the slightest visible alteration. The red coloration may in such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top.

9. *Carbonate of baryta* precipitates even in the cold all the iron as a basic salt mixed with hydrate of sesquioxide.

10. The reactions before the *blowpipe* are the same as with the protoxide.

§ 111.

Recapitulation and remarks. — On observing the behavior of the oxides of the fourth group with solution of potassa, it would appear that the separation of the oxide of zinc, which is soluble in an excess of this reagent, might be readily effected by its means; however, in the actual experiment, we find that in the presence of sesquioxide of iron, protoxide of cobalt, &c., some of the oxide of zinc precipitates with these oxides; and if only a small quantity of oxide of zinc is present, it frequently occurs that no trace of this metal can be detected in the alkaline filtrate.

Again, from the behavior of the different oxides with chloride of ammonium and an excess of ammonia, one would conclude that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also applied to the mixed oxides, is inaccurate, since greater or smaller portions of the other oxides will always precipitate with the sesquioxide of iron; and it may therefore happen that, in this process, small quantities of cobalt, manganese, &c., altogether escape detection.

It is far safer therefore to separate the other oxides of the fourth group from sesquioxide of iron by carbonate of baryta, as in that case the iron is precipitated free from oxide of zinc and protoxides of manganese and nickel, and mixed only with a very trifling quantity of protoxide of cobalt.

Protoxide of manganese may conveniently be separated from the protoxides of cobalt and nickel and from oxide of zinc, by treating the precipitated sulphides with moderately dilute acetic acid, which dissolves the sulphide of manganese, leaving the other sulphides unacted on. If the acetic acid solution is now mixed with solution of potassa, the least trace of a precipitate will be sufficient to recognise the manganese before the blowpipe with carbonate of soda.

If the sulphides left undissolved by acetic acid are now treated with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the fluid is then boiled, to expel the hydrosulphuric acid, and afterwards treated with solution of potassa or soda in excess, the zinc is sure to be detected in the filtrate by hydrosulphuric acid.

Cobalt may mostly be readily and safely detected in presence of nickel by the reaction with borax in the inner flame of the blowpipe. The detection of nickel in presence of cobalt is a less easy task, which may, however, be effected with great accuracy by three different methods. The *first* method is to add to the solution containing the two metals nitrate of

potassa in not too small proportion, then acetic acid to strongly acid reaction, and to let the mixture stand for at least several hours in a moderately warm place, when the cobalt will separate as nitrate of sesquioxide of cobalt and potassa; the nickel may then be readily precipitated from the filtrate by soda or sulphide of ammonium. The *second* method is to saturate with chlorine the very dilute solution of the two metals in hydrochloric acid, having the acid slightly in excess; add carbonate of baryta in excess, and let the fluid stand twenty-four hours. The cobalt is entirely precipitated in this process as black sesquioxide, whilst the nickel remains in solution, and may, after the removal of the baryta by sulphuric acid, be thrown down with solution of soda. The *third* method is based upon the application of cyanide of potassium. Both cyanide of nickel and cyanide of cobalt dissolve in cyanide of potassium; but cyanide of nickel is precipitated from this solution by acids, whilst cyanide of cobalt is not precipitated if the solution contains free hydrocyanic acid, and has been exposed to the action of heat.* This reaction, *i. e.*, the formation of a precipitate upon adding hydrochloric acid or dilute sulphuric acid to the solution of the two cyanides in cyanide of potassium, prepared under the conditions stated, indicates the presence of nickel. Whether the precipitate be cyanide of nickel or cobalticyanide of nickel, is quite immaterial as far as the *detection of nickel* is concerned: all we have to bear in mind is simply this, that no precipitate will form if cobalt alone is present in the solution, since cobalticyanide of potassium is not decomposed by hydrochloric acid. In order to get at the composition of the various precipitates which are formed by hydrochloric acid in solutions of the mixed cyanides of nickel and cobalt, and to comprehend the general process of their formation, we have to assume and consider three special and distinct cases, differing from one another in the relative proportions of nickel and cobalt which the solutions under examination respectively contain.

1, Ni : Co :: 3 eq. : 2 eq.
2, Ni : Co :: 3 eq. : 2 eq. + x
3, Ni : Co :: 3 eq. + x : 2 eq.

The solution will accordingly, in the first case, contain one eq. of cobalticyanide of potassium ($K_3, Co_2 Cy_6$) and 3 eq. of double cyanide of nickel and potassium 3 ($\bar{Ni}\,Cy, K\,Cy$); now upon the addition of hydrochloric acid in excess to this solution, the double cyanide of nickel and potassium suffers decomposition, and the potassium of the cobalticyanide of potassium transposes with the nickel of the cyanide of nickel: the products of this process of double decomposition and transposition are chloride of potassium, hydrocyanic acid, and cobalticyanide of nickel ($Ni_3, Co_2 Cy_6$), which latter separates in the form of a dirty-green precipitate containing the *whole* of the nickel and cobalt present in the solution. In the second case we obtain equally a precipitate of cobalticyanide of nickel; but this precipitate, though containing the whole of the *nickel*, does *not* contain *all* the *cobalt* of the solution, since the excess of cobalticyanide of potassium is not decomposed. In the third case, lastly, we obtain a precipitate of cobalticyanide of nickel, which contains

* In this process the double cyanide of cobalt and potassium (K Cy, Co Cy), which forms at first, is converted by the aid of the free hydrocyanic acid and the excess of cyanide of potassium, into cobalticyanide of potassium ($K_3, Co_2 Cy_6$) : 2 (Co Cy, K Cy) + K Cy + H Cy = ($K_3, Co_2 Cy_6$) + H.

the *whole* of the *cobalt* and a *portion* of the *nickel*, mixed with insoluble cyanide of nickel, which contains the rest of the nickel. The cobalticyanide of nickel has been formed here in the same manner as in the first case, whilst the cyanide of nickel owes its formation to the decomposition of the *excess* of the double cyanide of nickel and potassium. Hence it is evident that the presence of nickel is indispensable to the formation of a precipitate, and consequently that the production of a precipitate is the most positive proof of the presence of this metal.

Protoxide and sesquioxide of iron may be detected in presence of each other, by testing for the former with ferricyanide of potassium, for the latter with ferrocyanide of potassium or, better still, with sulphocyanide of potassium.

In conclusion, it is necessary to mention that alkalies fail to precipitate the oxides of the fourth group in presence of non-volatile organic substances (such as sugar, tartaric acid, &c.). We have already seen that the same applies to alumina.

§ 112.

SUPPLEMENT TO THE FOURTH GROUP.

SESQUIOXIDE OF URANIUM (U_2O_3).

Sesquioxide of uranium is brick-red, the hydrate is of a yellow color. Upon ignition both are converted into the dark blackish-green protosesquioxide. The solutions of sesquioxide of uranium in acids are yellow; hydrosulphuric acid does not alter them; sulphide of ammonium throws down after neutralization of the free acid, a dark brown precipitate of SULPHIDE OF URANIUM, which subsides slowly, and is readily soluble in acids, even in acetic acid, but does not dissolve in an excess of the precipitant. Ammonia, potassa, and soda produce yellow precipitates of sesquioxide of uranium and alkali, insoluble in excess of the precipitants. Carbonate of ammonia produces a yellow precipitate of carbonate of sesquioxide of uranium and ammonia, which *dissolves readily in an excess of the precipitant.* Potassa and soda throw down from the solution the whole of the sesquioxide of uranium. Carbonate of baryta completely precipitates solutions of sesquioxide of uranium, even in the cold. Ferrocyanide of potassium produces a reddish-brown precipitate: this is a very delicate test for uranium. Borax and phosphate of soda and ammonia give with sesquioxide of uranium in the inner flame of the blowpipe green beads, in the outer flame yellow beads, which upon cooling acquire a yellowish-green tint.

To separate sesquioxide of uranium from the other oxides of the fourth group, and from alumina, precipitate first with carbonate of baryta, which throws down the sesquioxide of iron, the sesquioxide of uranium, and the alumina, leaving the other oxides in solution. Dissolve the precipitate in hydrochloric acid, remove the baryta from the solution by means of sulphuric acid, filter, and add ammonia to the filtrate until a precipitate begins to form; add now a sufficient quantity of carbonate of ammonia, which has previously been once boiled, to destroy any bicarbonate of ammonia it may contain. Dilute with water and filter off the precipitate, which contains the whole of the sesquioxide of iron and alumina, the filtrate containing all the sesquioxide of uranium.

§ 113.

FIFTH GROUP.

OXIDE OF SILVER, SUBOXIDE OF MERCURY, OXIDE OF MERCURY, OXIDE OF LEAD, TEROXIDE OF BISMUTH, OXIDE OF COPPER, OXIDE OF CADMIUM.

Properties of the group.—The sulphides corresponding to the oxides of this group are insoluble both in dilute acids and in alkaline sulphides.* The solutions of these oxides are therefore completely precipitated by hydrosulphuric acid, no matter whether their reaction be neutral, alkaline, or acid.

For the sake of greater clearness and simplicity, we divide the oxides of this group into two divisions, and distinguish,

1. OXIDES PRECIPITABLE BY HYDROCHLORIC ACID, viz. : oxide of silver, suboxide of mercury, oxide of lead.

2. OXIDES NOT PRECIPITABLE BY HYDROCHLORIC ACID, viz. : oxide of mercury, oxide of copper, teroxide of bismuth, oxide of cadmium.

Lead must be considered in both divisions, since the sparing solubility of its chloride might lead to confounding its oxide with suboxide of mercury and oxide of silver, without affording us, on the other hand, any means of effecting its perfect separation from the oxides of the second division.

FIRST DIVISION OF THE FIFTH GROUP: OXIDES WHICH ARE PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

§ 114.

a. OXIDE OF SILVER (Ag O).

1. Metallic silver is white, very lustrous, moderately hard, highly malleable, ductile, rather difficultly fusible. It is not oxidized by ignition in the air. Nitric acid dissolves silver readily; the metal is insoluble in dilute sulphuric acid and in hydrochloric acid.

2. Oxide of silver is a grayish-brown powder; it is not altogether insoluble in water, and dissolves readily in dilute nitric acid. It forms no hydrate. It is decomposed by heat into metallic silver and oxygen gas.

3. The salts of oxide of silver are non-volatile and colorless; most of them acquire a black tint upon exposure to light. The soluble neutral salts do not alter vegetable colors, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* precipitate from solutions of salts of silver black SULPHIDE OF SILVER (Ag S), which is insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. Boiling nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. *Potassa* and *soda* precipitate from solutions of salts of silver the oxide of this metal in the form of a LIGHT BROWN POWDER, which is insoluble in an excess of the precipitant, but dissolves readily in ammonia.

* Consult, however, the paragraphs on oxide of copper and suboxide and oxide of mercury, as the latter remark applies only partially to them.

6. *Ammonia*, when added in very small quantity to neutral solutions of oxide of silver, throws down the *oxide* as a brown precipitate, which readily redissolves in an excess of ammonia. Acid solutions of silver are not precipitated.

7. *Hydrochloric acid* and *soluble metallic chlorides* produce in solutions of salts of silver a white, curdy precipitate of CHLORIDE OF SILVER ($Ag\,Cl$). In very dilute solutions these reagents impart simply a bluish-white opalescent appearance to the fluid. By the action of light chloride of silver first acquires a violet tint, and ultimately turns black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound the chloride of silver is again separated by acids. Concentrated hydrochloric acid and concentrated solutions of chlorides of the alkali metals dissolve some chloride of silver, more particularly upon application of heat; but the dissolved chloride separates again upon dilution. Upon exposure to heat, chloride of silver fuses without decomposition, giving upon cooling a transparent horny mass.

8. If compounds of silver, mixed with *carbonate of soda*, are exposed on a charcoal support to the *inner* flame of the blowpipe, WHITE, BRILLIANT, DUCTILE METALLIC GLOBULES are obtained, unattended with incrustation of the charcoal.

§ 115.

b. SUBOXIDE OF MERCURY ($Hg_2\,O$).

1. Metallic mercury is grayish-white, lustrous, fluid at the common temperature; it solidifies at $-40°$, and boils at $680°$ Fah. It is insoluble in hydrochloric acid; in dilute cold nitric acid it dissolves to nitrate of suboxide, in more concentrated hot nitric acid to nitrate of oxide of mercury.

2. Suboxide of mercury is a black powder which is readily soluble in nitric acid, and is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

3. The salts of suboxide of mercury volatilize upon ignition; most of them suffer decomposition in this process. Subchloride and subbromide of mercury volatilize unaltered. Most of the salts of suboxide of mercury are colorless. The soluble salts in the neutral state redden litmus paper. Nitrate of suboxide of mercury is decomposed by addition of much water into an insoluble basic and soluble acid salt.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce black precipitates of SUBSULPHIDE OF MERCURY ($Hg_2\,S$), which are insoluble in dilute acids, sulphide of ammonium, and cyanide of potassium. Protosulphide of sodium dissolves this subsulphide to sulphide, with separation of metallic mercury. Bisulphide of sodium dissolves the subsulphide to sulphide, without separation of metallic mercury. Subsulphide of mercury is readily decomposed and dissolved by nitrohydrochloric acid, but not by boiling concentrated nitric acids.

5. *Potassa* and *ammonia* produce in solutions of salts of suboxide of mercury black precipitates, which are insoluble in an excess of the precipitants. The precipitates produced by potassa consist of SUBOXIDE OF MERCURY; whilst those produced by ammonia consist of a BASIC DOUBLE SALT OF SUBOXIDE OF MERCURY AND AMMONIA, *e.g.* ($N\,H_3, N\,O_5 + 2\,Hg_2O$).

6. *Hydrochloric acid* and *soluble metallic chlorides* precipitate from solutions of salts of suboxide of mercury SUBCHLORIDE OF MERCURY

(Hg_2Cl), as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves, however, although very difficultly and slowly, upon long protracted boiling with these acids, being resolved by hydrochloric acid into chloride of mercury and metallic mercury, which separates; and converted by nitric acid into chloride of mercury and nitrate of oxide of mercury. Nitrohydrochloric acid and chlorine water dissolve the subchloride of mercury readily, converting it into chloride. Ammonia and potassa decompose the subchloride of mercury, and separate black suboxide from it.

7. If a drop of a neutral or slightly acid solution of suboxide of mercury is put on a *clean and smooth surface of copper*, and washed off after some time, the spot will afterwards, on being gently rubbed with cloth, paper, &c., appear WHITE and LUSTROUS like silver. The application of a gentle heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and thus removes the silvering.

8. *Protochloride of tin* produces in solutions of suboxide of mercury a gray precipitate of METALLIC MERCURY, which may be united into globules by boiling the metallic deposit, after decanting the fluid, with hydrochloric acid.

9. If an intimate mixture of an anhydrous compound of mercury with anhydrous *carbonate of soda* is introduced into a drawn-out glass tube, and covered with a layer of carbonate of soda, and the tube is then heated before the blowpipe, the mercurial compound invariably undergoes decomposition, and metallic mercury separates, forming a coat of gray sublimate above the heated part of the tube. The minute particles of mercury may be united into larger globules by rubbing this coating with a glass rod.

§ 116.

c. OXIDE OF LEAD (PbO).

1. Metallic lead is bluish-gray; its surface recently cut exhibits a metallic lustre; it is soft, malleable, readily fusible. Fused upon charcoal before the blowpipe, it forms a coating of yellow oxide on the charcoal. Hydrochloric acid and moderately concentrated sulphuric acid act upon it but little, even with the aid of heat; but dilute nitric acid dissolves it readily, more particularly on heating.

2. Oxide of lead is a yellow or reddish-yellow powder,* which upon exposure to a red heat fuses to a vitreous mass. Hydrated oxide of lead is white. Both the oxide and its hydrate dissolve readily in nitric and acetic acids.

3. The salts of oxide of lead are non-volatile; most of them are colorless; the neutral soluble salts redden litmus paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in solutions of salts of lead black precipitates of SULPHIDE OF LEAD (PbS), which are insoluble in *cold* dilute acids, in alkalies, alkaline sulphides, and cyanide of potassium. Sulphide of lead is decomposed by boiling concentrated nitric acid; the whole of the lead is first converted into nitrate of lead, and the greater part of the sulphur separates, whilst another portion is converted into sulphuric acid. The sulphuric acid thus

* While hot, the oxide of lead appears red.

formed decomposes a portion of the nitrate of lead, and forms with the liberated oxide sulphate of lead, which precipitates as a white powder ; the deposit in the solution consists therefore of a mixture of sulphate of lead and sulphur. In solutions of salts of lead containing an excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water or after neutralization of the free acid by an alkali. If a solution of lead is precipitated by hydrosulphuric acid, in presence of a large quantity of free hydrochloric acid, a red precipitate is formed, consisting of chloride and sulphide of lead, which, however, is converted by an excess of hydrosulphuric acid into black sulphide of lead.

5. *Potassa* and *ammonia* throw down BASIC SALTS OF LEAD in the form of white precipitates, which are insoluble in ammonia, and difficultly soluble in potassa. In solutions of acetate of lead ammonia does not immediately produce a precipitate, owing to the formation of a soluble triacetate of lead.

6. *Carbonate of soda* throws down from solutions of salts of lead a white precipitate of BASIC CARBONATE OF LEAD [*e.g.* $5\,(Pb\,O, C\,O_2) + Pb\,O, H\,O$], which is insoluble in an excess of the precipitant and also in cyanide of potassium.

7. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions of salts of lead heavy, white precipitates of CHLORIDE OF LEAD ($Pb\,Cl$), which are soluble in a large amount of water, especially upon application of heat. This chloride of lead is converted by ammonia into basic chloride of lead ($Pb\,Cl, 3\,Pb\,O + H\,O$), which is also a white powder, but almost absolutely insoluble in water. In dilute nitric and hydrochloric acids, chloride of lead is more difficultly soluble than in water.

8. *Sulphuric acid* and *sulphates* produce in solutions of salts of lead white precipitates of SULPHATE OF LEAD ($Pb\,O, S\,O_3$), which are nearly insoluble in water and dilute acids. From dilute solutions, especially from such as contain much free acid, the sulphate of lead precipitates only after some, frequently after a long time. It is advisable under all circumstances to add a considerable *excess* of dilute sulphuric acid, since sulphate of lead is more insoluble in this menstruum than in water. The separation of small quantities of sulphate of lead is best effected by evaporating, after the addition of the sulphuric acid, as far as practicable on the water-bath, and then treating the residue with water. Sulphate of lead is slightly soluble in concentrated nitric acid ; it dissolves with difficulty in boiling concentrated hydrochloric acid, but more readily in solution of potassa. It dissolves also pretty readily in the solutions of some of the salts of ammonia, particularly in solution of acetate of ammonia ; dilute sulphuric acid precipitates it again from these solutions.

9. *Chromate of potassa* produces in solutions of salt of lead a yellow precipitate of CHROMATE OF LEAD ($Pb\,O, Cr\,O_3$), which is readily soluble in potassa, but difficultly so in dilute nitric acid.

10. If a mixture of a compound of lead with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, soft, malleable METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered at the same time with a slight yellow incrustation of OXIDE OF LEAD.

§ 117.

Recapitulation and remarks.—The metallic oxides of the first division of the fifth group are most distinctly characterized in their corresponding chlorides; since the different respective deportment of these chlorides with water and ammonia affords us a simple means both of detecting them and effecting their separation from one another. For if the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or boiling water is repeatedly poured over it on the filter, the chloride of lead dissolves, whilst the chloride of silver and the subchloride of mercury remain undissolved. If these two chlorides are then treated with ammonia, the subchloride of mercury is converted into a black basic salt, insoluble in an excess of the ammonia; whilst the chloride of silver dissolves readily in that agent, and precipitates from this solution again upon addition of nitric acid. When operating upon small quantities, it is advisable first to expel the greater part of the ammonia by heat. In the aqueous solution of chloride of lead the metal may be readily detected by sulphuric acid.

SECOND DIVISION OF THE FIFTH GROUP: OXIDES WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

§ 118.

a. OXIDE OF MERCURY (Hg O).

1. Oxide of mercury is generally crystalline, and has a bright red color, which upon reduction to powder changes to a pale yellowish-red; the oxide precipitated from solutions of the nitrate of the oxide, or from solutions of the chloride, forms a yellow powder. Upon exposure to heat it transiently acquires a deeper tint; at a dull red heat it is resolved into metallic mercury and oxygen. Both the crystalline and non-crystalline oxide dissolve readily in hydrochloric and nitric acids.

2. The salts of oxide of mercury volatilize upon ignition; they suffer decomposition in this process; chloride, bromide, and iodide of mercury volatilize unaltered. Most of the salts of oxide of mercury are colorless. The soluble neutral salts redden litmus paper. The nitrate and sulphate of oxide of mercury are decomposed by water added in large quantity, into soluble acid and insoluble basic salts.

3. Addition of a very small quantity of *hydrosulphuric acid* or *sulphide of ammonium* produces in solutions of oxide of mercury, after shaking, a perfectly white precipitate. Addition of a somewhat larger quantity of these reagents causes the precipitate to acquire a yellow, orange, or brownish-red color, according to the less or greater proportion added; an excess of the precipitant produces a purely black precipitate of SULPHIDE OF MERCURY (Hg S). This progressive variation of color from white to black, which depends on the proportion of the hydrosulphuric acid or sulphide of ammonium added, distinguishes the oxide of mercury from all other bodies. The white precipitate which forms at first consists of a double compound of sulphide of mercury with the still undecomposed portion of the salt of oxide of mercury (in a solution of chloride of mercury, for instance, Hg Cl + 2 Hg S); the gradually in-

creasing admixture of black sulphide causes the precipitate to pass through the several gradations of color above mentioned. Sulphide of mercury is not dissolved by sulphide of ammonium, nor by potassa or cyanide of potassium; it is altogether insoluble in hydrochloric acid and in nitric acid, even upon boiling. It dissolves completely in sulphide of potassium, and is readily decomposed and dissolved by nitrohydrochloric acid.

4. *Potassa*, added in small quantity, produces in neutral or slightly acid solutions of oxide of mercury a reddish-brown precipitate, which acquires a yellow tint if the reagent is added in excess. The *reddish-brown* precipitate is a BASIC SALT; the *yellow* precipitate consists of OXIDE OF MERCURY. An excess of the precipitant does not redissolve these precipitates. In very acid solutions this reaction does not take place at all, or at least the precipitation is very incomplete. In presence of salts of ammonia, potassa produces in solutions of salts of oxide of mercury, instead of reddish-brown or yellow, *white* precipitates. The precipitate thrown down by potassa from a solution of chloride of mercury containing an excess of chloride of ammonium is of analogous composition to the precipitate produced by ammonia (see 5).

5. *Ammonia* produces in solutions of salts of oxide of mercury white precipitates quite analogous to those produced by potassa in presence of chloride of ammonium; thus, for instance, ammonia precipitates from solutions of chloride of mercury a double compound of chloride of mercury and amide of mercury ($Hg\,Cl + Hg\,N\,H_2$).

6. *Protochloride of tin*, added in small quantity to salts of oxide of mercury, reduces the oxide to suboxide, thus giving rise to the formation of a white precipitate of SUBCHLORIDE OF MERCURY ($Hg_2\,Cl$); but if added in excess, this reagent deprives the mercury completely of the oxygen and acid, or of the salt-radical, and throws it down in the metallic state, the same as in the case of the suboxide of mercury. The precipitate, which was white at first, acquires therefore now a gray tint, and may be readily united into globules of metallic mercury by boiling with hydrochloric acid.

7. The salts of oxide of mercury present the same deportment as the salts of the suboxide, both with metallic *copper* and when heated together with *carbonate of soda* in a glass tube before the blowpipe.

§ 119.

b. OXIDE OF COPPER (Cu O).

1. Metallic copper has a peculiar red color, and a strong lustre; it is moderately hard, malleable, ductile, rather difficultly fusible; in contact with water and air it becomes covered with a green crust of basic carbonate of oxide of copper; upon ignition in the air it becomes coated over with black oxide. In hydrochloric acid and dilute sulphuric acid it is insoluble or nearly so, even upon boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into sulphate of oxide of copper, with evolution of sulphurous acid.

2. Suboxide of copper is red, its hydrate yellow; both change to oxide upon ignition in the air. On treating the suboxide with dilute sulphuric acid, metallic copper separates, whilst sulphate of oxide of copper dissolves; on treating suboxide of copper with hydrochloric acid,

white subchloride of copper is formed, which dissolves in an excess of the acid, but is reprecipitated from this solution by water.

3. Oxide of copper is a black, fixed powder; its hydrate ($Cu\,O, H\,O$) is of a light blue color. Both the oxide of copper and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids.

4. Most of the neutral salts of oxide of copper are soluble in water; the soluble salts redden litmus, and suffer decomposition when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state; the hydrated salts are usually of a blue, or green color, which their solutions continue to exhibit even when much diluted.

5. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions of salts of oxide of copper, brownish-black precipitates of SULPHIDE OF COPPER ($Cu\,S$). This sulphide is insoluble in dilute acids and caustic alkalies. Hot solutions of sulphide of potassium and sulphide of sodium fail also to dissolve it or dissolve it only to a very trifling extent; but it is a little more soluble in sulphide of ammonium. The latter reagent is therefore not adapted to effect the perfect separation of sulphide of copper from other metallic sulphides. Sulphide of copper is readily decomposed and dissolved by boiling concentrated nitric acid; it dissolves completely in solution of cyanide of potassium. In solutions of salts of copper which contain an excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water.

6. *Potassa* or *soda* produces in solutions of salts of oxide of copper a light blue, bulky precipitate of HYDRATE OF OXIDE OF COPPER ($Cu\,O, H\,O$). If the solution is highly concentrated, and the potassa added in excess, the precipitate turns black after the lapse of some time, and loses its bulkiness, even in the cold; but the change takes place immediately if the precipitate is boiled with the fluid in which it is suspended (and which must, if necessary, be diluted for the purpose). In this process the ($Cu\,O, H\,O$) hydrated oxide is converted into the ($3\,Cu\,O, H\,O$) hydrated oxide.

7. *Carbonate of soda* produces in solutions of salts of oxide of copper a greenish-blue precipitate of HYDRATED BASIC CARBONATE OF COPPER ($Cu\,O, C\,O_2 + Cu\,O, H\,O$), which upon boiling changes to brownish-black oxide of copper, and dissolves in ammonia to an azure-blue, and in cyanide of potassium to a brownish fluid.

8. *Ammonia* added in small quantity to solutions of salts of oxide of copper produces a greenish-blue precipitate, consisting of a BASIC SALT OF COPPER. This precipitate redissolves readily upon further addition of ammonia, giving a perfectly clear solution of a magnificent azure-blue, which owes its color to the formation of a BASIC DOUBLE SALT OF AMMONIO-OXIDE OF COPPER. Thus, for instance, in a solution of sulphate of oxide of copper, ammonia produces a precipitate of $N\,H_3, Cu\,O + N\,H_4\,O, S\,O_3$. The blue color ceases to be perceptible only in very dilute solutions. Potassa produces in such blue solutions in the cold, after the lapse of some time, a precipitate of blue hydrate of oxide of copper; but upon boiling the fluid this reagent precipitates the whole of the copper as black oxide. Carbonate of ammonia presents the same deportment with salts of copper as pure ammonia.

9. *Ferrocyanide of potassium* produces even in moderately dilute solutions a reddish-brown precipitate of FERROCYANIDE OF COPPER (Cu_2, Cfy)

which is insoluble in dilute acids, but suffers decomposition when acted upon by potassa. In very highly dilute solutions the reagent produces only a reddish coloration of the fluid.

10. *Metallic iron* when brought into contact with concentrated solutions of salts of copper is almost immediately covered with a COPPERY-RED COATING OF METALLIC COPPER; very dilute solutions produce this coating only after some time. Presence of a little free acid accelerates the reaction.

If a fluid containing copper and a little free hydrochloric acid is poured into a small *platinum dish* (the lid of a platinum crucible), and a small piece of *zinc* is introduced, the bright platinum surface speedily becomes covered with a COATING OF COPPER; even with *very* dilute solutions this coating is clearly discernible.

11. If a mixture of a compound of copper with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, METALLIC COPPER is obtained, without simultaneous incrustation of the charcoal. The best method of freeing this copper from the particles of charcoal, is to triturate the fused mass in a small mortar with water, and to wash off the charcoal powder; when the coppery-red metallic particles will be left behind.

12. Copper, its alloys, and other compounds, when exposed to the *inner blowpipe flame*, impart an EMERALD GREEN tint to the outer flame. Addition of chloride of silver considerably heightens the delicacy of the reaction.

13. *Borax* and *phosphate of soda* and *ammonia* readily dissolve oxide of copper in the outer blowpipe flame. The beads are green while hot, blue when cold. In the inner flame the bead produced with borax appears colorless, that produced with phosphate of soda and ammonia turns dark green; both acquire a brownish-red tint upon cooling.

§ 120.

c. TEROXIDE OF BISMUTH ($Bi\,O_3$).

1. Bismuth has a reddish tin-white color and moderate metallic lustre; it is of medium hardness, brittle, readily fusible; when fused upon a charcoal support, it forms a coating of yellow teroxide on the surface of the charcoal. It dissolves readily in nitric acid, but is nearly insoluble in hydrochloric acid, and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into sulphate of teroxide of bismuth, with evolution of sulphurous acid.

2. The teroxide of bismuth is a yellow powder; when heated, it transiently acquires a deeper tint; it fuses at a red heat. Hydrate of teroxide of bismuth is white. Both the teroxide and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids.

3. The salts of bismuth are non-volatile, with the exception of a few (terchloride of bismuth). Most of them are decomposed at a red heat. They are colorless; some of them are soluble in water, whilst others are insoluble in this menstruum. The soluble salts, in the neutral state, redden litmus paper, and are decomposed into soluble acid and insoluble basic salts when treated with a large amount of water.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in neutral and acid solutions of salts of bismuth black precipitates of TERSULPHIDE OF BISMUTH ($Bi\,S_3$), which are insoluble in dilute acids, alkalies, alkaline

sulphides, and cyanide of potassium, but are readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of bismuth which contain a considerable excess of hydrochloric or nitric acid, hydrosulphuric acid produces a precipitate only after the addition of water.

5. *Potassa* and *ammonia* throw down from solutions of salts of bismuth HYDRATE OF TEROXIDE OF BISMUTH as a white precipitate, which is insoluble in an excess of the precipitant.

6. *Carbonate of soda* throws down from solutions of salts of bismuth BASIC CARBONATE OF BISMUTH ($Bi\ O_3$, $C\ O_2$) as a white bulky precipitate, which is insoluble in an excess of the precipitant, and equally so in cyanide of potassium.

7. *Chromate of potassa* precipitates from solutions of salts of bismuth CHROMATE OF BISMUTH as a yellow powder. This substance differs from chromate of lead in being soluble in dilute nitric acid and insoluble in potassa.

8. The reaction which characterizes the teroxide of bismuth more particularly, is the decomposition of its neutral salts by *water* into soluble acid and insoluble basic salts. The addition of a large amount of water to solutions of salts of bismuth causes the immediate formation of a dazzling white precipitate, provided there be not too much free acid present. This reaction is the most sensitive with terchloride of bismuth, as the basic chloride of bismuth ($Bi\ Cl_3$, $2\ Bi\ O_3$) is nearly insoluble in water. If water fails to produce a precipitate in nitric acid solutions of bismuth, owing to the presence of too much free acid, the excess of the acid must be removed by evaporation, before the water is added. From the basic salts of antimony which are formed under analogous circumstances, the precipitated basic salts of bismuth may be readily distinguished by their insolubility in tartaric acid.

9. If a mixture of a compound of bismuth with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle GLOBULES OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered at the same time with a slight yellow incrustation of TEROXIDE OF BISMUTH.

§ 121.

d. OXIDE OF CADMIUM ($Cd\ O$).

1. Metallic cadmium has a tin-white colour; it is lustrous, not very hard, malleable, ductile; it fuses at a temperature below red heat, and volatilizes at a temperature somewhat above the boiling point of mercury. Heated on charcoal before the blowpipe, it takes fire and burns, emitting brown fumes of oxide of cadmium, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it, with evolution of hydrogen; but nitric acid dissolves it most readily.

2. Oxide of cadmium is a yellowish-brown, fixed powder; its hydrate is white. Both the oxide and its hydrate dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The salts of oxide of cadmium are colorless or white; some of them are soluble in water. The soluble salts, in the neutral state, redden litmus paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions of salts of cadmium, bright yellow precipitates

of SULPHIDE OF CADMIUM (Cd S), which are insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. They are readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of cadmium which contain a considerable excess of acid, hydrosulphuric acid produces a precipitate only after dilution with water.

5. *Potassa* produces in solutions of salts of cadmium a white precipitate of HYDRATE OF OXIDE OF CADMIUM (Cd O, H O), which is insoluble in an excess of the precipitant.

6. *Ammonia* likewise precipitates from solutions of salts of cadmium white HYDRATE OF OXIDE OF CADMIUM, which, however, redissolves readily to a colorless fluid in an excess of the precipitant.

7. *Carbonate of potassa* and *carbonate of ammonia* produce white precipitates of CARBONATE OF CADMIUM (Cd O, C O_2), which are insoluble in an excess of the precipitants. The presence of salts of ammonia does not prevent the formation of these precipitates. The precipitated carbonate of cadmium dissolves readily in solution of cyanide of potassium. From dilute solutions the precipitate separates only after some time.

8. If a mixture of a compound of cadmium with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, the charcoal becomes covered with a reddish-brown coating of OXIDE OF CADMIUM, owing to the volatilization of the reduced metal and its subsequent re-oxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

§ 122.

Recapitulation and remarks.—The perfect separation of the metallic oxides of the second division of the fifth group from suboxide of mercury and oxide of silver may, as already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from oxide of lead. The oxide of mercury is distinguished from the other oxides of this division by the insolubility of the corresponding sulphide in boiling nitric acid. This property affords a convenient means for its separation. Moreover, the reactions with protochloride of tin or with metallic copper, as well as those in the dry way, will, after the previous removal of the suboxide, always readily indicate the presence of oxide of mercury.

From the still remaining oxides the oxide of lead is separated by addition of a sufficient quantity of dilute sulphuric acid; the separation is the most complete if the fluid, after the addition of the sulphuric acid, is evaporated on the water-bath, and the residue diluted with water. Teroxide of bismuth may be separated from oxide of copper and oxide of cadmium by addition of ammonia in excess, as the latter two oxides are soluble in an excess of this agent. If the filtered precipitate is dissolved in one or two drops of hydrochloric acid on a watchglass, and water added, the appearance of a milky turbidity is a confirmation of the presence of teroxide of bismuth.—The presence of a notable quantity of oxide of copper is revealed by the blue color of the ammoniacal solution; smaller quantities are detected by evaporating the ammoniacal solution nearly to dryness, adding a little acetic acid, and then ferrocyanide of potassium. The separation of oxide of copper from oxide of cadmium may be effected by means of carbonate of ammonia; however, by that method minute quantities of cadmium might readily escape detection.

The separation by means of cyanide of potassium is safer.—The process is very simple, being as follows: precipitate the solution with hydrosulphuric acid, let the precipitate settle, wash it slightly by decantation, and treat it with some cyanide of potassium, when the sulphide of copper will dissolve, the yellow sulphide of cadmium remaining undissolved.

§ 123.

SUPPLEMENT TO THE FIFTH GROUP.

Protoxide of Palladium (Pd O).

Palladium greatly resembles platinum; its color is somewhat darker. It fuses with great difficulty; when heated in the air to dull redness, it becomes covered with a blue coating; but, upon more intense ignition, it recovers its light color and metallic lustre. It is difficultly soluble in pure nitric acid, but dissolves somewhat more readily in nitric acid, containing nitrous acid; it dissolves very sparingly in boiling concentrated sulphuric acid, but readily in nitro-hydrochloric acid. It combines with 1 and 2 eq. of oxygen to form protoxide and binoxide. The latter, when heated with dilute hydrochloric acid, evolves chlorine, and gives solution of protochloride of palladium. Protoxide of palladium is black, its hydrate dark brown; both are, upon intense ignition, resolved into oxygen and metallic palladium. The salts of protoxide of palladium are mostly soluble in water; they are brown, or reddish-brown; their solutions, when concentrated, are reddish-brown; when dilute, yellow. Water precipitates from a solution of nitrate of protoxide of palladium containing a slight excess of acid, a brown-colored basic salt. The oxygen salts, as well as the protochloride, are decomposed upon ignition, leaving metallic palladium behind. Hydrosulphuric acid and sulphide of ammonium throw down from acid or neutral solutions of salts of protoxide of palladium, black protosulphide of palladium, which dissolves neither in sulphide of ammonium nor in boiling hydrochloric acid, and with difficulty in boiling nitric acid, but readily in nitro-hydrochloric acid. From the solution of the protochloride *potassa* precipitates a brown basic salt, soluble in an excess of the precipitant, *ammonia*, flesh-colored *ammonio-protochloride of palladium* (Pd Cl, NH_3), *cyanide of mercury*, yellowish-white gelatinous *protocyanide of palladium*, soluble in hydrochloric acid, and in ammonia. Protochloride of tin produces, in absence of free hydrochloric acid, a brownish-black precipitate; in presence of free hydrochloric acid, a red-colored solution, which speedily turns brown, and ultimately green, and, upon addition of water, brownish-red. Sulphate of protoxide of iron produces a deposit of palladium on the sides of the glass. Iodide of potassium precipitates black protiodide of palladium. Chloride of potassium precipitates from highly concentrated solutions of protoxide of palladium, potassio-protochloride of palladium (K Cl, Pd Cl), in form of golden-yellow needles, which dissolve readily in water giving a dark red fluid, but are insoluble in absolute alcohol.

§ 124.

SIXTH GROUP.

TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, TEROXIDE OF ANTIMONY, BINOXIDE OF TIN, PROTOXIDE OF TIN, ARSENIOUS ACID AND ARSENIC ACID.*

Properties of the group.—The sulphides corresponding to the oxides of the sixth group are insoluble in dilute acids. These combine with alkaline sulphides forming soluble sulphur salts, in which they perform the part of the acid. Hydrosulphuric acid precipitates these oxides therefore, like those of the fifth group, completely from acidified solutions. The precipitated sulphides differ, however, from those of the fifth group in this, that they dissolve in sulphide of ammonium, sulphide of potassium, &c., and are reprecipitated from these solutions on the addition of acids.

We divide the oxides of this group into two classes, and distinguish,

1. OXIDES WHOSE CORRESPONDING SULPHIDES ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, and are reduced to the metallic state upon fusion in conjunction with nitrate and carbonate of soda: viz., teroxide of gold and binoxide of platinum.

2. OXIDES WHOSE CORRESPONDING SULPHIDES ARE SOLUBLE IN BOILING HYDROCHLORIC ACID OR NITRIC ACID, and are upon fusion with nitrate and carbonate of soda converted into oxides or acids, which combine with the soda: viz., Teroxide of antimony, protoxide and binoxide of tin, arsenious and arsenic acids.

FIRST DIVISION.

Special Reactions.

§ 125.

a. TEROXIDE OF GOLD ($Au\,O_3$).

1. Metallic gold has a reddish yellow color, and a high metallic lustre: it is rather soft, exceedingly malleable, ductile, difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids; but it dissolves in fluids containing or evolving chlorine, *e.g.* in nitro-hydrochloric acid. The solution contains terchloride of gold.

2. Teroxide of gold is a blackish-brown, its hydrate a chesnut-brown powder. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little teroxide of gold; water reprecipitates it from these solutions.

3. Salts of gold with oxygen acids are nearly unknown. The haloid salts of gold are yellow, and their solutions continue to exhibit this color up to a high degree of dilution. The whole of them are readily decom-

* I have placed the two acids of arsenic with the metallic oxides, since the deportment of the sulphides of arsenic might readily lead to their being confounded with some of the oxides of the sixth group, and because in the systematic course of analysis the sulphide of arsenic is invariably obtained in the same precipitate with the sulphide of antimony, the sulphide of tin, &c.

posed upon ignition. Neutral solution of terchloride of gold reddens litmus paper.

4. *Hydrosulphuric acid* precipitates from neutral and acid solutions of gold the whole of the metal as black TERSULPHIDE OF GOLD ($Au\ S_3$), which is insoluble in either of the acids, partly soluble in potassa, and perfectly so in sulphuretted alkaline sulphides and in nitro-hydrochloric acid. From boiling solutions hydrosulphuric acid throws down metallic gold.

5. *Sulphide of ammonium* produces the same precipitate. This redissolves in an excess of the precipitant only if the latter contains an excess of sulphur.

6. *Ammonia* produces, but only in tolerably concentrated solutions of gold, reddish-yellow precipitates of AURATE OF AMMONIA (fulminating gold). The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. *Protochloride of tin* containing an admixture of bichloride produces even in extremely dilute solutions of gold, a purple-red precipitate (or coloration at least), which sometimes inclines rather to violet or to brownish-red. This precipitate, which has received the name of PURPLE OF CASSIUS, is insoluble in hydrochloric acid. It is assumed to be a hydrated compound of binoxide of tin and protoxide of gold with protoxide and binoxide of tin ($Au\ O,\ Sn\ O_2 + Sn\ O,\ Sn\ O_2 + 4\ H\ O$).

8. *Salts of protoxide of iron* reduce the teroxide of gold, when added to its solutions, and precipitate metallic gold in form of a most minutely divided brown powder, which shows metallic lustre when pressed with the blade of a knife, or when rubbed. The fluid in which the precipitate is suspended appears of a blackish-blue color by transmitted light.

§ 126.

b. BINOXIDE OF PLATINUM ($Pt\ O_2$).

1. Metallic platinum has a light steel-gray color; it is very lustrous, moderately hard, very malleable and ductile, difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids. It dissolves in nitro-hydrochloric acid, especially upon heating. The solution contains bichloride of platinum.

2. Binoxide of platinum is a blackish-brown, its hydrate a reddish-brown powder. Both are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids.

3. The salts of binoxide of platinum are decomposed at a red heat. They are yellow; bichloride of platinum is reddish-brown, its solution reddish-yellow, which tint it retains up to a high degree of dilution. The solution reddens litmus paper. Exposure to a very low red heat converts bichloride of platinum to protochloride; application of a stronger red heat reduces it to the metallic state. Solution of bichloride of platinum, containing protochloride, has a deep dark brown color.

4. *Hydrosulphuric acid* throws down from acid and neutral solutions —(but not from alkaline solutions, or, at all events, not completely)— after the lapse of some time a blackish-brown precipitate of BISULPHIDE OF PLATINUM ($Pt\ S_2$). If the solution is heated after the addition of the hydrosulphuric acid the precipitate forms *immediately.* It dissolves in a great excess of alkaline sulphides, more particularly of the higher degrees of sulphuration. Bisulphide of platinum is insoluble in

hydrochloric acid and in nitric acid; but it dissolves in nitrohydrochloric acid.

5. *Sulphide of ammonium* produces the same precipitate; this redissolves completely in a large excess of the precipitant, if the latter contains an excess of sulphur. Acids reprecipitate the bisulphide of platinum unaltered from this solution.

6. *Potassa and ammonia* produce in not too highly dilute solutions of salts of platinum, mixed with some hydrochloric acid, yellow crystalline precipitates of POTASSIO- and AMMONIO-BICHLORIDE OF PLATINUM, which are insoluble in acids, but dissolve in an excess of the precipitants upon application of heat. From dilute solutions these precipitates are obtained by evaporating the fluid mixed with potassa or ammonia (or chloride of potassium or chloride of ammonium), but remaining still acid, on the water-bath to dryness, and treating the residue with dilute spirit of wine until the alkaline chlorides are dissolved. Upon ignition, ammonio-bichloride of platinum leaves spongy platinum behind. Potassio-bichloride leaves platinum and chloride of potassium.

7. *Protochloride of tin* imparts to solutions of salts of binoxide of platinum which contain much free hydrochloric acid an INTENSELY DARK BROWNISH-RED COLOR, owing to a reduction of the binoxide or bichloride of platinum to protoxide or simple chloride. But the reagent produces no precipitate in such solutions.

8. *Sulphate of protoxide of iron* does not precipitate solution of bichloride of platinum.

§ 127.

Recapitulation and remarks.—The reactions of gold and platinum enable us, at least partially, to detect these two metals in the presence of many other oxides, and also when platinum and gold are present in the same solution. In the latter case the solution is either evaporated to dryness with chloride of ammonium, and the residue treated with spirit of wine, in order to obtain the gold in solution, and the platinum in the residue; or the gold is precipitated with protochloride of iron, and the fluid filtered off after standing some time. The presence of the platinum in the filtrate may then be proved by means of chloride of ammonium, after previous evaporation and addition of spirit of wine. The latter method is applicable only in cases where both metals are in solution as chlorides.

SECOND DIVISION OF THE SIXTH GROUP.

Special Reactions.

§ 128.

a. PROTOXIDE OF TIN (SnO).

1. Tin has a light gray-white color and a high metallic lustre; it is soft and malleable; when bent, it produces a crackling sound. When heated in the air, it absorbs oxygen, and is converted into grayish-white binoxide; heated on charcoal before the blowpipe, it forms a white coating on the support. Concentrated hydrochloric acid dissolves tin to protochloride, with evolution of hydrogen gas; nitrohydrochloric acid dissolves it, according to circumstances, to bichloride or to a mixture of proto- and bichloride. Tin dissolves with difficulty in dilute sulphuric acid; concentrated sulphuric acid converts it, with the aid of heat, into sulphate of binoxide; moderately concentrated nitric acid oxidizes it

readily, particularly with the aid of heat; the white binoxide formed does not redissolve in an excess of the acid.

2. Protoxide of tin is a black or grayish-black powder; its hydrate is white. Protoxide of tin is reduced by fusion with cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into binoxide of tin, which is insoluble in an excess of the acid.

3. The salts of protoxide of tin are colorless, and are decomposed by heat. The soluble salts, in the neutral state, redden litmus paper. The salts of protoxide of tin rapidly absorb oxygen from the air, and are partially or entirely converted into salts of binoxide; hence a solution of protochloride of tin becomes speedily turbid (from ensuing separation of oxybichloride of tin), if the glass is often opened and there is only little free acid present; hence it is only quite recently prepared protochloride of tin which will completely dissolve in water free from air, &c.

4. *Hydrosulphuric acid* throws down from neutral and acid solutions of salts of protoxide of tin a dark brown precipitate of hydrated PROTOSULPHIDE OF TIN (Sn S), which is insoluble, or nearly so, in protosulphide of ammonium, but dissolves readily in the higher yellow sulphide. Acids precipitate from this solution yellow bisulphide of tin, mixed with sulphur. Protosulphide of tin dissolves also in solution of soda or potassa. Acids precipitate from these solutions brown protosulphide. Boiling hydrochloric acid dissolves it, with evolution of hydrogen; boiling nitric acid converts it into insoluble binoxide of tin. Alkaline solutions of protosalts of tin are not, or at least only imperfectly, precipitated by hydrosulphuric acid.

5. *Sulphide of ammonium* produces the same precipitate of hydrated PROTOSULPHIDE OF TIN.

6. *Potassa, ammonia, carbonate of potassa,* and *carbonate of ammonia* produce in solutions of salts of protoxide of tin a white, bulky precipitate of HYDRATE OF PROTOXIDE OF TIN (Sn O, H O), which redissolves readily in an excess of potassa, but is insoluble in an excess of the other three precipitants. If the solution of hydrate of protoxide of tin in potassa is briskly evaporated, a compound of binoxide of tin and potassa is formed, which remains in solution, whilst metallic tin precipitates; but, upon evaporating slowly, crystalline anhydrous protoxide of tin separates.

7. *Terchloride of gold* produces in solutions of protochloride or protoxide of tin, upon addition of some nitric acid (without application of heat), a precipitate or coloration of PURPLE OF CASSIUS. (Compare § 125, 7.)

8. Solution of *chloride of mercury,* added in excess, produces in solutions of protochloride or protoxide of tin a white precipitate of SUBCHLORIDE OF MERCURY, owing to the protosalt of tin withdrawing from the chloride of mercury half of its chlorine.

9. If a fluid containing protoxide or protochloride of tin is added to a mixture of *ferricyanide of potassium* and *sesquichloride of iron,* a precipitate of *Prussian blue* separates immediately, owing to the reduction of the ferricyanide. This reaction, which was first pointed out by Löwenthal, is extremely delicate, but it can be held to be decisive only in cases where no other reducing agent is present.

10. If compounds of protoxide of tin, mixed with *carbonate of soda* and some *borax,* or, better still, with a mixture of equal parts of *carbonate of soda* and *cyanide of potassium,* are exposed on a charcoal support to the *inner blowpipe flame,* malleable grains of METALLIC TIN are obtained. The best way of making quite sure of the real nature of these

grains, is to triturate them and the surrounding parts of charcoal with water in a small mortar, pressing heavily upon the mass; then to wash the charcoal off from the metallic particles. Upon strongly heating the grains of metallic tin on a charcoal support, the latter becomes covered with a coating of white binoxide.

§ 129.

b. Binoxide of Tin ($Sn\,O_2$).

1. Binoxide of tin is a powder varying in color from white to straw-yellow, and which upon heating transiently assumes a brown tint. It forms two different series of salts with acids, bases, and water. The hydrate precipitated by alkalies from solution of bichloride of tin dissolves readily in hydrochloric acid; whilst that formed by the action of nitric acid upon tin—hydrate of metastannic acid—remains undissolved. But if it is boiled for some time with hydrochloric acid, it takes up acid; if the excess of the acid is then poured off, and water added, a clear solution is obtained. Upon boiling this solution, hydrate of metastannic acid separates from it; whilst from a solution of bichloride, largely diluted with water, common hydrate of binoxide separates upon boiling.

2. The salts of binoxide of tin are colorless; they are decomposed at a red heat. The soluble salts of binoxide of tin, in the neutral state, redden litmus paper. Bichloride of tin is a volatile liquid, strongly fuming in the air.

3. *Hydrosulphuric acid* throws down from all acid and neutral solutions of salts of binoxide of tin, particularly upon heating, a *white* flocculent precipitate, if the solution of the binoxide is in excess; a *faintly yellow* precipitate, if the hydrosulphuric acid is in excess. The former (the white precipitate) may safely be assumed, in the case of a solution of bichloride of tin, to consist of a mixture of bichloride and bisulphide of tin (however, it has not as yet been analysed); the latter (the yellow precipitate) consists of hydrated BISULPHIDE OF TIN ($Sn\,S_2$). Alkaline solutions are not precipitated by hydrosulphuric acid. The bisulphide of tin dissolves readily in potassa, alkaline sulphides, and concentrated boiling hydrochloric acid. It dissolves with some difficulty in pure ammonia, and is altogether insoluble in carbonate of ammonia. Nitric acid converts it into insoluble binoxide of tin. It is insoluble in a heated solution of acid sulphite of potassa and sulphurous acid. Upon deflagrating bisulphide of tin with nitrate and carbonate of soda, sulphate of soda and binoxide of tin are obtained. If a solution of bisulphide of tin in potassa is boiled with teroxide of bismuth, tersulphide of bismuth and binoxide of tin are formed, which latter substance remains dissolved in the potassa solution.

4. *Sulphide of ammonium* produces the same precipitate of hydrated BISULPHIDE OF TIN; the precipitate redissolves readily in an excess of the precipitant. From this solution acids reprecipitate the bisulphide of tin unaltered.

5. *Potassa* and *ammonia, carbonate of soda* and *carbonate of ammonia,* produce in solutions of salts of binoxide of tin white precipitates which, according to the nature of the solutions, consist of hydrate of binoxide of tin, or of hydrate of metastannic acid. Both dissolve readily in an excess of potassa.

6. *Sulphate of soda, nitrate of ammonia* (in fact, most neutral salts), when added in excess, throw down from solutions of both modifications

of binoxide of tin, provided they are not too acid, the whole of the tin as HYDRATED BINOXIDE OF HYDRATED METASTANNIC ACID.

7. *Metallic zinc* precipitates from solutions of bichloride or of salts of binoxide of tin, in the absence of free acid, white, gelatinous hydrate of binoxide; but in presence of a sufficient quantity of free hydrochloric acid, METALLIC TIN, in the shape of small gray scales, or as a spongy mass. If the operation is conducted in a platinum dish, no blackening of the latter is observed (difference between tin and antimony).

8. The compounds of the binoxide of tin manifest the same deportment before the blowpipe as those of the protoxide. Binoxide of tin is also readily reduced when fused with cyanide of potassium in a glass tube.

§ 130.

c. TEROXIDE OF ANTIMONY ($Sb\,O_3$).

1. Metallic antimony has a bluish tin-white color and is very lustrous; it is hard, brittle, readily fusible. When heated on charcoal before the blowpipe, it emits thick white fumes of teroxide of antimony, which form a coating on the charcoal; this combustion continues for some time, even after the removal of the metal from the flame; it is the most distinctly visible if a current of air is directed with the blowpipe directly upon the sample on the charcoal. But if the sample on the support is kept steady, that the fumes may ascend straight, the metallic grain becomes surrounded with a net of brilliant crystals of teroxide of antimony. Nitric acid oxidizes antimony readily: the dilute acid converting it almost entirely into teroxide, the more concentrated acid into antimonic acid; both are nearly insoluble in nitric acid; still in the acid fluid filtered from the precipitate there are always found traces of antimony. Hydrochloric acid, even boiling, does not attack antimony. In nitrohydrochloric acid the metal dissolves readily. The solution contains terchloride of antimony ($Sb\,Cl_3$), or pentachloride of antimony ($Sb\,Cl_5$), according to the degree of concentration of the acid and the duration of the action.

2. According to the different modes of its preparation, teroxide of antimony occurs either in the form of white, brilliant crystalline needles, or as a grayish-white powder. It fuses at a moderate red heat; when exposed to a higher temperature, it volatilizes without decomposition. It is almost insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. Teroxide of antimony is easily reduced to the metallic state by fusion with cyanide of potassium.

3. Antimonic acid ($Sb\,O_5$) is pale yellow; its hydrates are white. Both the acid and its hydrates redden litmus paper; they are slightly soluble in water, and insoluble in nitric acid, but dissolve pretty readily in hot concentrated hydrochloric acid: the solution contains pentachloride of antimony ($Sb\,Cl_5$), and turns turbid upon addition of water. Upon ignition, antimonic acid loses oxygen, and is converted into antimonate of teroxide of antimony ($Sb\,O_3$, $Sb\,O_5$). Of the antimonates the potassa and ammonia salts alone are soluble in water: acids precipitate hydrate of antimonic acid from the solutions, chloride of sodium throws down from them antimonate of soda (§ 89, 2).

4. Part of the salts of teroxide of antimony are decomposed upon ignition; the haloid salts volatilize readily and unaltered. The soluble neutral salts of antimony redden litmus paper. When treated with

a large amount of water, they are decomposed into insoluble basic and soluble acid salts. Thus, for instance, water throws down from solutions of terchloride of antimony in hydrochloric acid, a white bulky precipitate of basic terchloride of antimony (powder of Algaroth) $Sb\,Cl_3$, $5\,Sb\,O_3$, which after some time becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and therefore prevents its formation if mixed with the solution previously to the addition of the water. It is by this property that the basic terchloride of antimony is distinguished from the basic salts of bismuth formed under similar circumstances.

5. *Hydrosulphuric acid* precipitates from acid solutions of teroxide of antimony the whole of the metal as orange-red TERSULPHIDE OF ANTIMONY ($Sb\,S_3$). In alkaline solutions this reagent fails to produce a precipitate or, at least, it precipitates them only imperfectly; neutral solutions also are only imperfectly thrown down by it. The tersulphide of antimony produced is readily dissolved by potassa and by alkaline sulphides, especially if the latter contain an excess of sulphur; it is but sparingly soluble in ammonia, and—if it contains no free sulphur nor pentasulphide of antimony—almost insoluble in bicarbonate of ammonia. It is insoluble in dilute acids. Concentrated boiling hydrochloric acid dissolves it, with evolution of hydrosulphuric acid gas. It is not dissolved by heating with an aqueous solution of acid sulphite of potassa and sulphurous acid. When heated in the air, it is converted into a mixture of antimonate of teroxide of antimony with tersulphide of antimony. When deflagrated with nitrate of soda, it gives sulphate and antimonate of soda. If a potassa solution of tersulphide of antimony is boiled with teroxide of bismuth, tersulphide of bismuth precipitates, and teroxide of antimony dissolved in potassa remains in the solution. On fusing tersulphide of antimony with cyanide of potassium, metallic antimony and sulphocyanide of potassium are produced. If the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbonic acid gas (see § 131, 12), no sublimate of antimony is produced. But if a mixture of tersulphide of antimony with carbonate of soda or with cyanide of potassium and carbonate of soda, is heated in a glass tube in a stream of hydrogen gas (compare § 131, 4), a mirror of antimony is deposited on the inner surface of the tube, immediately behind the spot occupied by the mixture.

From a solution of antimonic acid in hydrochloric acid, sulphuretted hydrogen throws down pentasulphide of antimony ($Sb\,S_5$), which dissolves readily when heated with solution of soda or ammonia, and equally so in concentrated boiling hydrochloric acid, with evolution of hydrosulphuric acid gas and separation of sulphur.

6. *Sulphide of ammonium* produces in solutions of teroxide of antimony an orange-red precipitate of TERSULPHIDE OF ANTIMONY, which readily redissolves in an excess of the precipitant if the latter contains an excess of sulphur. Acids throw down from this solution pentasulphide of antimony ($Sb\,S_5$). However, the orange color appears in that case usually of a lighter tint, owing to an admixture of free sulphur.

7. *Potassa, ammonia, carbonate of potassa*, and *carbonate of ammonia* throw down from solutions of terchloride of antimony, and also of simple salts of teroxide of antimony—but not, or at least not immediately, from solutions of tartar emetic or analogous compounds—a white, bulky precipitate of TEROXIDE OF ANTIMONY, which redissolves pretty readily in an excess of potassa, but requires the application of heat for its

re-solution in carbonate of potassa, and is alogether insoluble in ammonia.

8. *Metallic zinc* precipitates from all solutions of teroxide of antimony, if they contain no free nitric acid, METALLIC ANTIMONY as a black powder. If a few drops of a solution of antimony, containing some free hydrochloric acid, are poured into a platinum dish (the inside of a platinum crucible cover), and a small piece of zinc introduced, hydrogen is evolved and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions: these new reactions I can therefore recommend as being delicate and characteristic. Cold hydrochloric acid fails to remove the stain, which, however, may be immediately removed by warm nitric acid.

9. If a solution of teroxide of antimony in solution of potassa or soda is mixed with solution of *nitrate of silver*, a deep black precipitate of SUBOXIDE OF SILVER forms with the grayish-brown precipitate of oxide of silver. Upon now adding ammonia in excess, the oxide is redissolved, whilst the suboxide is left undissolved (*H. Rose*). The following equation will explain the formation of the suboxide of silver in this process: $K\,O, Sb\,O_3 + 4\,Ag\,O = K\,O, Sb\,O_5 + 2\,Ag_2\,O$. This exceedingly delicate reaction affords us an excellent means of detecting teroxide of antimony in presence of antimonic acid.

10. If a solution of teroxide of antimony is introduced into a flask in which hydrogen gas is being evolved from pure *zinc* and dilute *sulphuric acid*, the zinc oxidizes not only at the expense of the oxygen of the water, but also at the expense of that of the teroxide of antimony, and the antimony separates accordingly in the metallic state; but a portion of the metal combines in the moment of its separation with the liberated hydrogen of the water, forming ANTIMONETTED HYDROGEN GAS ($Sb\,H_3$). If this operation is conducted in a gas-evolution flask, connected by means of a perforated cork with the limb of a bent tube of which the other limb ends in a finely drawn-out point, pinched off at the top,* and the hydrogen passing through the fine aperture of the tube is ignited after the atmospheric air is completely expelled, the flame appears of a bluish-green tint, which is imparted to it by the antimony separating in a state of intense ignition upon the combustion of the antimonetted hydrogen; white fumes of teroxide of antimony rise from the flame, which condense readily upon cold substances, forming spots on them which are not dissolved by water. But if a cold body, a porcelain dish, for instance, is now depressed upon the flame, METALLIC ANTIMONY is deposited upon the surface of the plate, in a state of the most minute division, forming a deep black and almost lustreless spot. If the middle part of the tube through which the gas is passing is heated to redness, the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated part.

As the acids of arsenic give under the same circumstances similar spots of metallic arsenic, it is always necessary to examine the spots produced, in order to ascertain whether they really consist of antimony or contain any of that metal. With spots deposited on a porcelain dish the object in view is most readily attained by treating them with a solution of chloride of soda (a compound of hypochlorite of soda with chloride of sodium, pre-

* In accurate experiments it is advisable to use *Marsh's* apparatus. (§ 131, 10).

pared by mixing a solution of chloride of lime with carbonate of soda in excess, and filtering); which will immediately dissolve arsenical spots, leaving the spots proceeding from antimony untouched, or, at least, removing them only after a very protracted action. A mirror within the glass tube, on the other hand, may be tested by heating it whilst the current of hydrogen gas still continues to pass through the tube: if the mirror volatilizes only at a higher temperature, and the hydrogen gas then issuing from the tube does not smell of garlic; if it is only with a strong current that the ignited gas deposits spots on porcelain, and the mirror before volatilizing fuses to small lustrous globules distinctly discernible through a magnifying glass,—the presence of antimony may be considered certain. Or, better still, the metals may be identified by conducting through the tube a *very slow* stream of dry hydrosulphuric acid gas, and heating the mirror, by means of a spirit-lamp, proceeding from the outer to the inner border, and accordingly in an opposite direction to that of the gaseous current. The antimonial mirror is by this means converted into tersulphide of antimony, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of dry hydrochloric acid gas is now transmitted through the glass tube, the tersulphide of antimony, if present in thin layers only, disappears immediately; if the incrustation is somewhat thicker, it takes a short time to dissipate it. The reason for this is, that the tersulphide of antimony decomposes readily with hydrochloric acid, and the terchloride of antimony formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now conducted into some water, the presence of antimony in the latter fluid may readily be proved by means of hydrosulphuric acid. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals.

11. If a mixture of a compound of antimony with *carbonate of soda and cyanide of potassium* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle globules of METALLIC ANTIMONY are produced, which may be readily recognised by the peculiar appearances attendant upon their oxidation (compare § 130, 1).

§ 131.

d. Arsenious Acid ($As\,O_3$).

1. Metallic arsenic has a blackish-gray color and high metallic lustre, which it retains in dry air, but loses in moist air, becoming covered with suboxide; the metallic arsenic of commerce looks therefore rather dull, the planes of crystallization appearing bronze-colored and feebly shining. Arsenic is not very hard, but very brittle: at a dull red heat it volatilizes without fusion. The fumes have a most characteristic odor of garlic, which proceeds from the suboxide of arsenic formed. Heated with free access of air, arsenic burns—at an intense heat with a bluish flame—emitting white fumes of arsenious acid, which condense on cold bodies. If arsenic is heated in a glass tube sealed at the lower end, the greater part of it volatilizes unoxidized, and recondenses above the heated spot as a lustrous black sublimate (arsenical mirror); a very thin coating of the sublimate appears of a brownish-black color. In contact with air and water arsenic oxidizes slowly to arsenious acid. Weak nitric acid converts it, with the aid of heat, into arsenious acid, which dissolves only

sparingly in an excess of the acid; strong nitric acid converts it partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid; concentrated boiling sulphuric acid oxidizes it to arsenious acid, with evolution of sulphurous acid.

2. Arsenious acid generally presents the appearance either of a transparent vitreous or of a white porcelain-like mass. Triturated, it gives a heavy, white, gritty powder. When heated, it volatilizes in white inodorous fumes. If the operation is conducted in a glass tube, a sublimate is obtained consisting of small brilliant octahedrons and tetrahedrons. Arsenious acid is only difficultly moistened by water; it comports itself in this respect like a fatty substance. It is difficultly soluble in cold, but more readily in hot water. It is copiously dissolved by hydrochloric acid, as well as by solution of soda and potassa. Upon boiling with nitrohydrochloric acid it dissolves to arsenic acid. It is highly poisonous.

3. The arsenites are mostly decomposed upon ignition either into arsenates and metallic arsenic, which volatilizes, or into arsenious acid and the base with which it was combined. Of the arsenites those only with alkaline bases are soluble in water. The insoluble arsenites are dissolved, or at least decomposed, by hydrochloric acid. Terchloride of arsenic is a colorless, volatile liquid, fuming in the air, which allows the addition of a little water, but is decomposed by a larger amount into arsenious acid, which partly separates, and hydrochloric acid, which retains the rest of the arsenious acid in solution.

4. *Hydrosulphuric acid* precipitates solutions of arsenious acid and of neutral arsenites slowly and imperfectly, except a free acid be present, in which case the precipitation is immediate and perfect. Alkaline solutions are not precipitated. The precipitates are of a bright yellow color; they consist of TERSULPHIDE OF ARSENIC ($As\,S_3$), and are readily and completely dissolved by pure alkalies, alkaline carbonates and bicarbonates, and also by alkaline sulphides; but they are nearly insoluble in hydrochloric acid, even when concentrated and boiling. Boiling nitric acid decomposes and dissolves them readily. The deflagration of tersulphide of arsenic with carbonate of soda and nitrate of soda gives rise to the formation of arsenate and sulphate of soda. If a solution of tersulphide of arsenic in potassa is boiled with hydrated carbonate or basic nitrate of teroxide of bismuth, tersulphide of bismuth and arsenite of potassa are produced.

If recently precipitated tersulphide of arsenic is digested with sulphurous acid and acid sulphite of potassa, the precipitate is dissolved; upon heating the solution to boiling, the fluid turns turbid, owing to the separation of sulphur, which upon continued boiling is for the greater part redissolved. The fluid contains, after expulsion of the sulphurous acid, arsenite and hyposulphite of potassa ($2\,As\,S_3 + 8(K\,O, S\,O_2) = 2\,K\,O, As\,O_3 + 6\,K\,O, S_2\,O_2 + S_3 + 7\,S\,O_2$). Tersulphide of antimony and bisulphide of tin do not show this reaction, as I have already stated (§ 129, 3 and § 130, 5) (*Bunsen*).

If a mixture of tersulphide of arsenic with from 3 to 4 parts of carbonate of soda is made into a paste with some water, and this spread over small glass splinters, and after being well dried, rapidly heated to redness in a glass tube through which dry hydrogen gas is transmitted, a large portion of the arsenic present is reduced to the metallic state and expelled, if the temperature applied is sufficiently high. Part of the

reduced arsenic forms a metallic mirror on the inner surface of the tube, the remainder is carried away suspended in the hydrogen gas; the minute particles of arsenic impart a bluish tint to the flame when the gas is kindled, and form stains of arsenic upon the surface of a porcelain dish depressed upon the flame. The fusion of the mixture of tersulphide of arsenic with carbonate of soda first gives rise to the formation of a double tersulphide of arsenic and sulphide of sodium, and of arsenite of soda ($2\,As\,S_3 + 4\,Na\,O, C\,O_2 = 3\,Na\,S, As\,S_3 + Na\,O, As\,O_3 + 4\,C\,O_2$). Upon heating these products the arsenite of soda is resolved into arsenic and arsenate of soda ($5\,As\,O_3 = 2\,As + 3\,As\,O_5$), and the tersulphide of arsenic and sulphide of sodium into arsenic and pentasulphide of arsenic and sulphide of sodium ($5\,As\,O_3 = 2\,As + 3\,As\,O_5$); and by the action of the hydrogen the arsenate of soda is also converted into hydrate of soda, arsenic, and water. With the exception, therefore, of that portion of the arsenic which constitutes a component part of the double pentasulphide of arsenic and sulphide of sodium formed in the process, a sulphur salt which is not decomposed by hydrogen; all the arsenic is expelled (*H. Rose*).

This method of reduction gives indeed very accurate results, but it does not enable us to distinguish arsenic from antimony with a sufficient degree of certainty, nor to detect the one in presence of the other. (Compare § 130, 5.)

The operation is conducted in the apparatus illustrated by

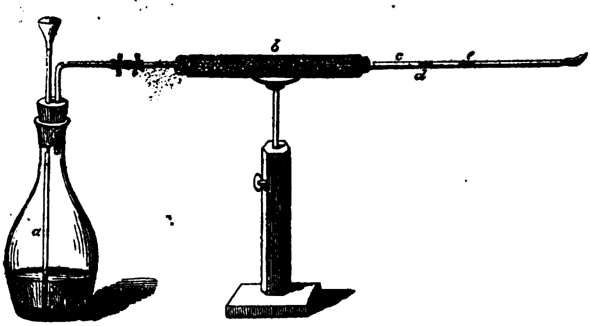


Fig. 22.

a is the evolution flask, *b* a tube containing chloride of calcium, *c* the tube in which, at the point *d*, the glass splinter with the mixture of tersulphide of arsenic and carbonate of soda is placed; this tube is made of difficultly fusible glass free from lead. When the apparatus is completely filled with pure hydrogen gas, *d* is exposed to a gentle heat at first, in order to expel all the moisture which may still be present, and then suddenly to a very intense heat,* to prevent the sublimation of undecomposed tersulphide of arsenic. The metallic mirror is deposited near the point *e*. Another method of effecting the reduction of tersulphide of arsenic to the metallic state, and which combines with the very highest degree of delicacy the advantage of precluding the possibility of confounding arsenic with antimony, will be found described in number 12.

5. *Sulphide of ammonium* also causes the formation of TERSULPHIDE OF ARSENIC. In neutral and alkaline solutions, however, the tersulphide

* The flame of the blowpipe answers the purpose best.

formed does not precipitate, but remains dissolved as a double sulphide of arsenic and ammonium (tersulphide of arsenic and sulphide of ammonium). From this solution it precipitates immediately upon the addition of a free acid.

6. *Nitrate of silver* leaves aqueous solutions of arsenious acid perfectly bright, or at least produces only a trifling yellowish-white turbidity in them; but if a little ammonia is added, a yellow precipitate of ARSENITE OF SILVER ($3\,Ag\,O$, $As\,O_3$) separates. The same precipitate forms, of course, immediately upon the addition of nitrate of silver to the solution of a neutral arsenite. The precipitate dissolves readily in nitric acid as well as in ammonia, and is not insoluble in nitrate of ammonia; if therefore a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, as it remains dissolved in the nitrate of ammonia formed.

7. *Sulphate of copper* produces under the same circumstances as the nitrate of silver a yellowish-green precipitate of ARSENITE OF COPPER.

8. If to a solution of arsenious acid in an excess of concentrated solution of soda or potassa, or to the solution of an alkaline arsenite mixed with *caustic potassa* or *soda* a few drops of a dilute solution of sulphate of copper are added, a clear, blue fluid is obtained, which upon boiling deposits a red precipitate of SUBOXIDE OF COPPER, leaving arsenate of potassa in solution. This reaction is exceedingly delicate, provided not too much of the solution of sulphate of copper be used. Even should the red precipitate of suboxide of copper be so exceedingly minute as to escape detection by transmitted light, yet it will always be discernible with great distinctness upon looking in at the top of the test tube. Of course this reaction, although really of great importance in certain instances, as a confirmatory proof of the presence of arsenious acid, and more particularly also as a means of distinguishing that acid from arsenic acid, is yet entirely inapplicable for the *direct detection* of arsenic, since grape sugar and other organic substances also produce suboxide of copper from salts of oxide of copper in the same manner.

9. If a solution of arsenious acid mixed with hydrochloric acid is heated with a clean slip of *copper*, an IRON-GRAY film of metallic arsenic is deposited on the copper, even in *highly dilute* solutions; when this film increases in thickness, it peels off in black scales. If the coated copper slip is heated with solution of ammonia, the film peels off from the copper, and separates in form of minute spangles (*Reinsch*). Let it be observed that these are not pure arsenic, but always contain copper, and will accordingly never completely volatilize. Upon heating them in a tube containing air, arsenious acid sublimes.

10. If an acid or neutral solution of arsenious acid or any of its compounds is mixed with *zinc*, *water*, and *sulphuric acid*, ARSENETTED HYDROGEN ($As\,H_3$) is formed, in the same manner as compounds of antimony give under analogous circumstances antimonetted hydrogen. (Compare § 130, 10.) This reaction affords us a most delicate test for the detection of even the most minute quantities of arsenic.

The operation is conducted in the apparatus illustrated by Fig. 23, or in one of similar construction.* *a* is the evolution flask; *b* a bulb intended to receive the water carried along with the gaseous current; *c* a

* I willingly adopt the very convenient form of *Marsh's* apparatus recommended by *Otto* in his excellent *Manual of Chemistry.*

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tube filled with cotton and small lumps of chloride of calcium to remove water. This tube is connected with *b* and *d* by vulcanized india-rubber; *d* should have an inner diameter of 7 millimètres (see Fig. 24), and must

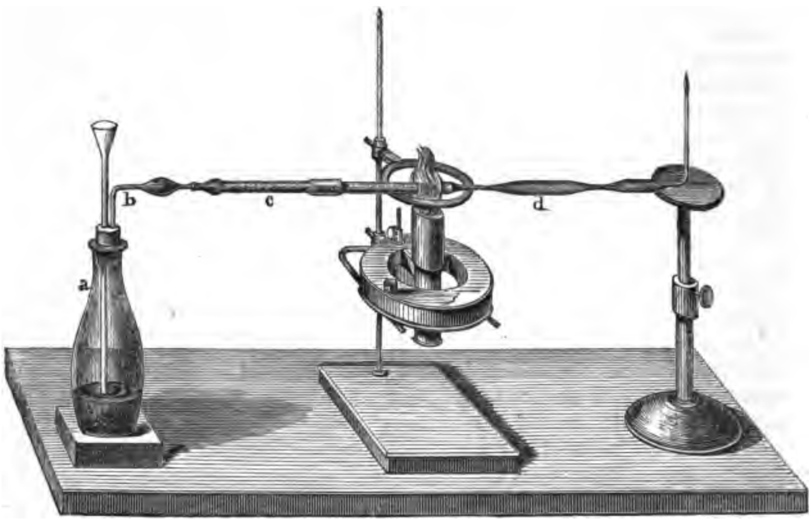

Fig. 23.

be made of difficultly fusible glass free from lead. In experiments requiring great accuracy the tube should be drawn out as shown in Fig. 23. The operation is now commenced by evolving in *a* a moderate and uniform current of hydrogen gas, from pure granulated zinc and concentrated sulphuric acid diluted with 3 parts of water. When the evolution of hydrogen has proceeded for some time, so that it may safely be concluded the air has been completely expelled from the apparatus, the gas is kindled at the open end of the tube *d*. It is advisable to wrap a piece of cloth round the flask before kindling the gas, to guard against accidents in case of an explosion. It is now absolutely necessary first to ascertain whether the zinc and the sulphuric acid are quite free from any admixture of arsenic. This is done by depressing a porcelain dish horizontally upon the flame to make it spread over the surface: if the hydrogen contains arsenetted hydrogen, brownish or brownish-black stains of arsenic will appear on the porcelain; the non-appearance of such stains may be considered as a proof of the freedom of the zinc and sulphuric acid from arsenic. In very accurate experiments, however, additional evidence is required to ensure the positive certainty of the purity of the reagents employed; for this purpose the part of the tube *d*, shown in Fig. 23, is heated to redness with a *Berzelius* or gas-lamp, and kept some time in a state of ignition: if no arsenical coating makes its appearance in the narrowed part of the tube, the reagents employed may be pronounced free from arsenic, and the operation proceeded with, by pouring the fluid to be tested for arsenic through the funnel tube into the

Fig. 24.

flask, and afterwards some water to rinse the tube. Only a very little of the fluid ought to be poured in at first, as in cases where the quantity of arsenic present is considerable, and a somewhat large supply of the fluid is poured into the flask, the evolution of gas often proceeds with such violence as to stop the further progress of the experiment.

Now if the fluid contains arsenic, there is immediately evolved, with the hydrogen, arsenetted hydrogen, which at once imparts a bluish tint to the flame of the kindled gas, owing to the combustion of the particles of arsenic separating from the arsenetted hydrogen in passing through the flame. At the same time white fumes of arsenious acid arise, which condense upon cold objects. If a porcelain plate is now depressed upon the flame, the separated and not yet reoxidized arsenic condenses upon the plate in black stains, the same way as antimony. (See § 130, 10.) The stains formed by arsenic incline, however, more to a blackish-brown tint, and show a bright metallic lustre: whilst the antimonial stains are of a deep black color and but feebly lustrous. The arsenical stains may be distinguished moreover from the antimonial stains by solution of chloride of soda (compare § 130, 10), which will at once dissolve arsenical spots, leaving antimonial spots unaffected, or removing them only after a considerable time.

If the heat of a *Berzelius*, or gas-lamp, is now applied to the part of the tube *d*, shown in Fig. 23, a brilliant arsenical mirror makes its appearance in the narrowed portion of the tube behind the heated part; this mirror is of a darker and less silvery white hue than that produced by antimony under similar circumstances; from which it is, moreover, distinguished by the facility with which it may be dissipated in a current of hydrogen gas without previous fusion, and by the characteristic odor of garlic emitted by the escaping (unkindled) gas. If the gas is kindled whilst the mirror in the tube is being heated, the flame will, even with a very weak current of gas, deposit arsenical stains on a porcelain plate.

The reactions and properties just described are amply sufficient to enable us to distinguish between arsenical and antimonial stains and mirrors; but they will often fail to detect arsenic with positive certainty in presence of antimony. Now, in cases of this kind, the following process will serve to set at rest all possible doubt as to the presence or absence of arsenic:—

Heat the long tube through which the arsenetted hydrogen passes to redness in several parts, to produce distinct metallic mirrors; then transmit through the tube a very weak stream of dry hydrosulphuric acid gas, and heat the metallic mirrors with a common spirit-lamp, proceeding from the outer towards the inner border. If arsenic alone is present, yellow tersulphide of arsenic is formed inside the tube; if antimony alone is present, an orange-red or black tersulphide of antimony is produced; and if the mirror consisted of both metals, the two sulphides appear side by side, the sulphide of arsenic as the more volatile lying invariably before the sulphide of antimony. It you now transmit through the tube containing the sulphide of arsenic, sulphide of antimony, or both sulphides together, dry hydrochloric gas, without applying heat, no alteration will take place if sulphide of arsenic alone is present, even though the gas be transmitted through the tube for a considerable time. If sulphide of antimony alone is present, this will

entirely disappear, as already stated, and if both sulphides are present, the sulphide of antimony will immediately volatilize, whilst the yellow sulphide of arsenic will remain. If a small quantity of ammonia is now drawn into the tube, the sulphide of arsenic is dissolved, and may thus be readily distinguished from sulphur which perhaps may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

Marsh was the first who suggested the method of detecting arsenic by the production of arsenetted hydrogen.

11. If a small lump of arsenious acid (*a*) be introduced into the pointed end of a drawn-out glass tube (Fig. 25) and a fagment of very recently burnt charcoal (*b*) pushed down the tube to within a short distance of the arsenious acid, and the flame of a spirit-lamp applied, first to the piece of charcoal, then to the arsenious acid, a MIRROR OF METALLIC ARSENIC will form at *c*, owing to the reduction of the arsenious acid vapor by the red-hot charcoal. If the tube be now cut between *b* and *c*, and then heated in an inclined position, with the cut end *c* turned upwards, the metallic mirror will volatilize, emitting the characteristic odor of garlic. This is both the simplest and safest way of detecting pure arsenious acid.

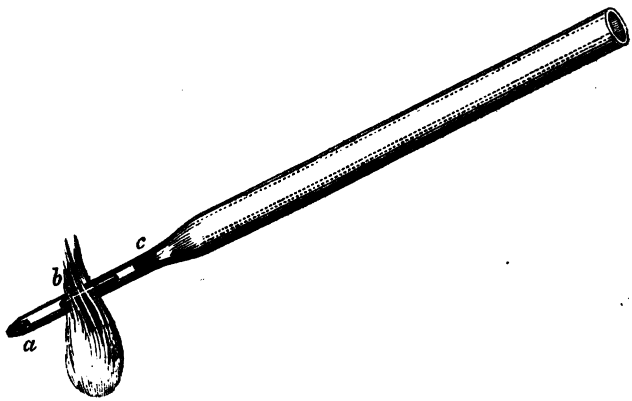

Fig. 25.

12. If arsenites, or arsenious acid, or tersulphide of arsenic are fused together with a mixture of equal parts of dry *carbonate of soda* and *cyanide of potassium*, the whole of the arsenic is reduced to the metallic state, and so is the base also, if easily reducible; the eliminated oxygen converts part of the cyanide of potassium into cyanate of potassa. In the reduction of tersulphide of arsenic, sulphocyanide of potassium is formed. The operation is conducted as follows:—introduce the perfectly dry arsenical compound into the bulb of a small bulb-tube (Fig. 26), and cover it with six times the quantity of a perfectly dry mixture of equal parts of carbonate of soda and cyanide of potassium. The whole quantity must not much more than half-fill the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. Heat the bulb now gently with a gas or spirit-lamp; should some water still escape upon gently heating the mixture, wipe the inside of the tube *perfectly dry* with a

twisted slip of paper. It is of the highest importance for the success of the experiment to bestow great care upon the expulsion of the water, drying the mixture, and wiping the tube clean and dry. Apply now a strong heat to the bulb, to effect the reduction of the arsenical compound, and continue this for awhile, as the arsenic often requires

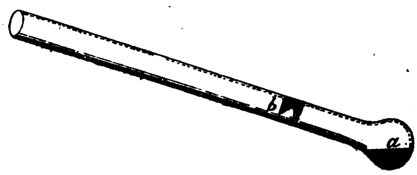

Fig. 26.

some time for its complete sublimation. The mirror, which is deposited at *b*, is of exceeding purity. It is obtained from all arsenites whose bases remain either altogether untouched, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by it, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for the direct production of arsenic from tersulphide of arsenic, and is in this respect superior in simplicity and accuracy to all other methods hitherto suggested. The delicacy of the reaction may be very much heightened by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by *Dr. V. Babo* and myself has shown that the most accurate and satisfactory results are obtained in the following manner:—

Figs. 27 and 28 show the apparatus in which the process is conducted.

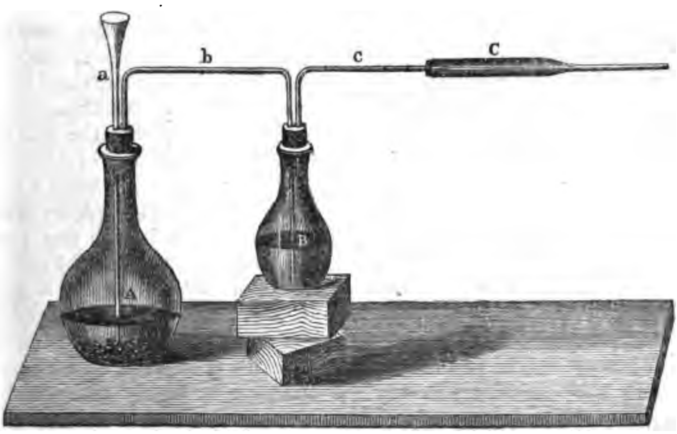

Fig. 27.

A is a capacious flask intended for the evolution of carbonic acid; it is half-filled with water and lumps of solid limestone or marble (not

chalk, as this would not give a constant stream of gas). *B* is a smaller flask containing concentrated sulphuric acid. The flask *A* is closed with a double-perforated cork, into the one aperture of which is inserted a funnel-tube (*a*), which reaches nearly to the bottom of the flask; into the other perforation is fitted a tube (*b*), which serves to conduct the evolved gas into the sulphuric acid in *B*, where it is thoroughly freed from moisture. The tube *c* conducts the dried gas into the reduction-tube *C*, of which Fig. 28 gives a representation on the scale of one-third of the actual length. The tubes which I employ for the purpose in my own experiments, have an inner diameter of eight millimètres.

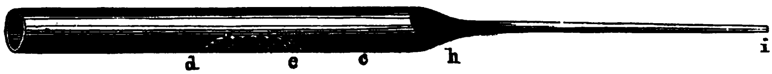

Fig. 28.

When the apparatus is fully prepared for use, triturate the perfectly dry sulphide of arsenic, or arsenite in a slightly heated mortar with about twelve parts of a well-dried mixture consisting of three parts of carbonate of soda and one part of cyanide of potassium. Put the powder upon a narrow slip of card-paper bent into the shape of a gutter, and push this into the reduction-tube down to *e*; turn the tube now half-way round its axis, which will cause the mixture to drop into the tube between *e* and *d*, every other part remaining perfectly clean. Connect the tube now with the gas-evolution apparatus, and evolve a moderate stream of carbonic acid, by pouring some hydrochloric acid into the flask *A*. Heat the tube *C* in its whole length very gently with a spirit-lamp, until the mixture in it is quite dry; when every trace of water is expelled, and the gas-stream has become so slow that the single bubbles pass through the sulphuric acid in *B* at intervals of one second, heat the reduction-tube to redness at *c*, by means of a spirit or gas-lamp; when *c* is red-hot, apply the flame of a second gas or larger spirit-lamp to the mixture, proceeding from *d* to *e*, until the whole of the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses at *h*, whilst a small portion only escapes through *i*, imparting to the surrounding air the peculiar odor of garlic. Advance the flame of the second lamp slowly and gradually up to *c*, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven to *h*. When you have effected this, close the tube at the point *i* by fusion, and apply heat, proceeding from *i* towards *h*, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner perfectly distinct mirrors of arsenic may be produced from as little as the $\frac{1}{300}$th part of a grain of tersulphide of arsenic. No mirrors are obtained by this process from tersulphide of antimony, nor from any other compound of antimony.

13. If arsenious acid or one of its compounds is exposed on a charcoal support to the *reducing flame of the blowpipe*, a highly characteristic garlic odor is emitted, more especially if some carbonate of soda is added to the examined sample. This odor has its origin in the reduction and re-oxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others that are based upon the mere indications of the sense of smell, cannot be implicitly relied on.

§ 132.

e. Arsenic Acid ($As\,O_5$).

1. Arsenic acid is a transparent or white mass, which gradually deliquesces in the air, and dissolves slowly in water. It fuses at a gentle red heat without suffering decomposition; but at a higher temperature it is resolved into oxygen, and arsenious acid, which volatilizes. It is highly poisonous.

2. Most of the arsenates are insoluble in water. Of the so-called neutral arsenates those with alkaline bases alone are soluble in water. Most of the neutral and basic arsenates can bear a strong red heat without suffering decomposition. The acid arsenates lose their excess of acid upon ignition, the free acid being resolved into arsenious acid and oxygen.

3. *Hydrosulphuric acid* fails to precipitate alkaline and neutral solutions of arsenates; but in acidified solutions it produces a yellow precipitate of PENTASULPHIDE OF ARSENIC ($As\,S_5$). This precipitate never forms instantaneously, and in dilute solutions frequently only after the lapse of a considerable time (twenty-four hours, for instance). Heat promotes its separation. The pentasulphide of arsenic manifests the same deportment as the tersulphide with the various solvents and decomposing agents mentioned in the preceding paragraph. If a solution of arsenic acid, or of an arsenate, is mixed with sulphurous acid, or with sulphite of soda and some hydrochloric acid, the sulphurous acid is converted into sulphuric acid, and the arsenic acid reduced to arsenious acid; application of heat promotes the change. If hydrosulphuric acid is now added, the whole of the arsenic is thrown down as tersulphide.

4. *Sulphide of ammonium* converts the arsenic acid in neutral and alkaline solutions of arsenates into pentasulphide of arsenic, which remains in solution as ammonio-pentasulphide of arsenic (pentasulphide of arsenic and sulphide of ammonium). Upon the addition of an acid to the solution, this double sulphide is decomposed, and pentasulphide of arsenic precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions of arsenates are precipitated with hydrosulphuric acid. It is promoted by heat.

5. *Nitrate of silver* produces under the circumstances stated § 131, 6, a highly characteristic reddish-brown precipitate of ARSENATE OF SILVER ($3\,Ag\,O, As\,O_5$), which is readily soluble in dilute nitric acid and in ammonia, and dissolves also slightly in nitrate of ammonia. Accordingly, if a little of the precipitate is dissolved in a large proportion of nitric acid, neutralization with ammonia often fails to reproduce the precipitate.

6. *Sulphate of copper* produces under the circumstances stated § 131, 7, a greenish-blue precipitate of ARSENATE OF COPPER ($2\,Cu\,O, H\,O, As\,O_5$).

7. With *zinc* in presence of sulphuric acid, with *copper*, with *cyanide of potassium*, and before the *blowpipe*, the compounds of arsenic acid comport themselves in the same way as those of arsenious acid. If the reduction of arsenic acid by zinc is effected in a platinum dish, the platinum does not turn black, as is the case in the reduction of antimony by zinc (§ 130, 8).

8. If a solution of arsenic acid, or of an arsenate soluble in water, is

added to a clear mixture of *sulphate of magnesia*, *chloride of ammonium*, and a sufficient quantity of *ammonia*, a crystalline precipitate of ARSENATE OF AMMONIA AND MAGNESIA ($2\,Mg\,O, N\,H_4\,O, As\,O_5 + 12$ aq.) separates; from concentrated solutions immediately, from dilute solutions after some time.

§ 133.

Recapitulation and remarks.—I have again made the separation and positive identification of the oxides belonging to the second division of the sixth group the object of a most careful study, and my endeavors have been crowned with complete success. I will here describe first the different ways best adapted to effect the detection or separation of tin, antimony, and arsenic, when present together in the same compound or mixture, and afterwards the most reliable means of distinguishing between the several oxides of each of the three metals.

1. If you have a mixture of sulphide of tin, sulphide of antimony, and sulphide of arsenic, triturate 1 part of it, together with 1 part of dry carbonate of soda, and 1 part of nitrate of soda, and transfer the mixed powder gradually to a small porcelain crucible containing 2 parts of nitrate of soda kept in a state of fusion at a not over-strong heat; oxidation of the sulphides ensues, attended with slight deflagration. The fused mass contains binoxide of tin, arsenate and antimonate of soda, with sulphate, carbonate, nitrate, and nitrite of soda. You must take care not to raise the heat to such a degree, nor continue the fusion so long, as to lead to a reduction of the nitrite of soda to the caustic state. Treat the fused mass, poured out upon a piece of porcelain, with *cold* water until it is completely softened; then filter the fluid off from the undissolved residue, which contains the binoxide of tin and antimonate of soda nearly unacted on. Mix the filtrate, which contains the arsenate of soda and the other salts, with nitric acid to distinctly acid reaction, then with a sufficient proportion of solution of nitrate of silver; a precipitate of chloride of silver forms (if the reagents employed or the precipitated sulphides contained a chlorine compound) and some nitrite of silver. Filter, and carefully add to the filtrate dilute solution of ammonia, whereupon the characteristic reddish-brown precipitate of arsenate of oxide of silver will make its appearance, first in the uppermost stratum of the fluid where the solution of ammonia comes first into contact with it, but subsequently, upon complete neutralization of the free acid, in every part of the fluid.

Wash now the filter containing the residuary binoxide of tin and antimonate of soda once with water, then three times with a mixture of equal parts of water and spirit of wine, dry, incinerate,* and put the ash into a tube of difficultly fusible glass, sealed at one end, measuring some eight or ten centimètres in length, and having an inner diameter of from five to seven millimètres; add to the ash in the tube four times the quantity of cyanide of potassium, and heat over a *Berzelius* or gas-lamp.† This effects the reduction of the binoxide of tin and

* With small quantities of substance this may be done most conveniently by twisting the little filter together, inserting it into a spiral coil of platinum wire, and holding this in the outer mantle of a flame.

† Had not the nitrate of soda been removed by washing, as directed, this part of the process would be attended with an explosion.

antimonic acid, and a fused mass is produced which appears gray from the minutely divided reduced metals in it. If the tube is now dipped whilst still red-hot into a test-tube filled with cold water, the part containing the fused mass will crack off, and the broken fragments sink to the bottom of the water. Upon application of heat, the fused mass will readily dissolve, leaving the metals behind, which may now by repeated boiling with water and decantation be freed from the last traces of other matters still adhering to them. Heat the residuary metallic mass with hydrochloric acid just to the boiling point, when the tin or a portion of it will dissolve to protochloride, with evolution of hydrogen gas; by means of chloride of mercury or a mixture of ferricyanide of potassium and sesquichloride of iron you may now easily, and with positive certainty, detect the protochloride of tin in the solution, even though only a minute trace of the metal be present. Upon heating the residue remaining in the tube repeatedly with hydrochloric acid, the whole, or nearly the whole of the tin present is dissolved out, and the black-colored antimony alone is left undissolved. Upon heating this residue with hydrochloric acid, with addition of one or two drops of nitric acid, it dissolves, and if you now add to the solution hydrosulphuric acid, an orange-colored precipitate of tersulphide of antimony is obtained. If only slight traces of antimony are present, the color of this precipitate is not very distinct, owing to imperfect separation from the tin. Let, therefore, the precipitate of the impure tersulphide of antimony settle, decant the clear fluid, dissolve the precipitate in a little boiling hydrochloric acid, concentrate the solution somewhat, and then test in the lid of a platinum crucible with zinc, which will at once remove all doubt, showing even the minutest trace of antimony.

2. Instead of incinerating the filter with the binoxide of tin and antimonate of soda, you may also dissolve the precipitate on it in a little hot hydrochloric acid, wash the filter with water, concentrate the fluid somewhat, and test with zinc in a small platinum dish, when the antimony will at once reveal its presence by staining the platinum brownish-black; to detect the tin, wait until the little slip of zinc is almost entirely dissolved, then decant the fluid, heat the residue with some hydrochloric acid, and test the solution for protochloride of tin as in 1.

3. If the quantity of binoxide of tin and antimonate of soda is somewhat larger, the two bodies may be separated also by boiling with concentrated solution of soda, which dissolves the binoxide of tin, leaving the antimonate of soda unaffected. It is advisable to add, after the process of boiling, some spirit of wine, say about $\frac{1}{4}$ by volume of the entire fluid, to guard against the antimonate of soda being dissolved; for the same reason the precipitate must be washed with equal volumes of water and spirit of wine. If the alkaline solution is now evaporated to drive off the spirit of wine, hydrochloric acid then added, and lastly, hydrosulphuric acid, the tin is precipitated as sulphide; the antimony may in like manner be precipitated from the solution of the antimonate of soda in hydrochloric acid.

4. If the mixed sulphides are treated with fuming hydrochloric acid, the sulphide of antimony and sulphide of tin dissolve, whilst the sulphide of arsenic is left nearly altogether undissolved. If the residuary sulphide of arsenic is treated with ammonia, and the solution obtained evaporated, after adding to it a very little carbonate of soda, an arsenical mirror may readily be produced from the residue with cyanide of potassium and

carbonate of soda in a stream of carbonic acid gas. The solution, which contains the tin and antimony, may be treated as directed in 2. Or, if there is a considerable excess of antimony, the solution may be mixed with sesquicarbonate of ammonia in excess, and boiled. A considerable proportion of the antimony present dissolves in this process, whilst binoxide of tin mixed with a small quantity of teroxide of antimony remains undissolved. The presence of the tin may now be the more readily proved by the method given in 1 (*Bloxam*).

5. If sulphide of antimony, sulphide of tin, and sulphide of arsenic are dissolved in sulphide of potassium, a *large* excess of a concentrated solution of sulphurous acid added, the mixture digested for some time in the water-bath, then boiled until all sulphurous acid is expelled, and filtered, the filtrate contains all the arsenic as arsenious acid (which may be precipitated from it by hydrosulphuric acid), whilst tersulphide of antimony and bisulphide of tin are left behind undissolved (*Bunsen*). After dissolving the residue in hydrochloric acid, the antimony and tin may be detected as directed in 2.

6. In the analysis of alloys, binoxide of tin and teroxide of antimony are often obtained together as a residue insoluble in nitric acid. If the quantities are considerable, the teroxide of antimony may be extracted with tartaric acid, and the solution tested for it with hydrosulphuric acid; the binoxide of tin may be reduced with cyanide of potassium. For minute quantities I recommend the method described in 1. An absolute separation of the two oxides may be effected by fusing them with hydrate of soda in a silver crucible, treating the mass with water, and adding one-third (by volume) of spirit of wine. The binoxide of tin is by this means obtained in solution as a compound of binoxide of tin and soda, whilst the antimonate of soda is left undissolved (*H. Rose*).

7. For the most accurate way of separating antimony and arsenic, and distinguishing between the two metals, viz., by treating with hydrosulphuric acid the mirror produced by *Marsh's* method, and separating the resulting sulphides by means of hydrochloric acid gas, I refer to § 131, 10. Antimony and arsenic may, however, when mixed together in form of hydrides, be separated also in the following way: Conduct the gases mixed with an excess of hydrogen, first through a tube containing glass splinters moistened with solution of acetate of lead, to retain the hydrochloric and hydrosulphuric gas, then in a slow stream into a solution of nitrate of silver. All the antimony in the gas falls down as black antimonide of silver, whilst the arsenic remains in solution as arsenious acid, and may, after precipitation of the excess of silver by hydrochloric acid, be readily detected in the fluid.

Protoxide and *binoxide of tin* may be detected and identified in presence of each other, by testing one portion of the solution containing both oxides for the protoxide with chloride of mercury, terchloride of gold or a mixture of ferricyanide of potassium and sesquichloride of iron, and another portion for the binoxide, by pouring it into a concentrated solution of soda.

Teroxide of antimony in presence of *antimonic acid* may be identified by the reaction described in § 130, 9. *Antimonic acid* in presence of *teroxide of antimony*, by heating the teroxide suspected to contain an admixture of the acid, but without any other admixture, with hydrochloric acid free from chlorine, and iodide of potassium free from iodate of potassa. If antimonic acid is present, iodine will separate, which, in

the case of larger quantities of acid, may be known from the brown color exhibited by the fluid, in the case of only slight traces of acid, after addition of a few drops of bisulphide of carbon (see § 154, 10). (*Bunsen.*)

Arsenious acid and *arsenic acid* in the same solution may be distinguished by means of nitrate of silver. If the precipitate contains little arsenate and much arsenite of silver, it is necessary, in order to identify the former, to add cautiously and drop by drop most highly dilute nitric acid, which dissolves the yellow arsenite of silver first.

A still safer way to detect small quantities of arsenic acid in presence of arsenious acid, is to precipitate the solution which contains the two acids, with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia. The precipitate formed may be further examined by dissolving it in a very small quantity of nitric acid, mixing the solution with nitrite of silver, and then very cautiously adding dilute ammonia, which will lead to the formation of a precipitate of brownish-red arsenate of silver, if arsenic acid is present. Arsenious acid in presence of arsenic acid may also be identified by the reduction of oxide of copper effected by its agency. To distinguish between the ter- and the pentasulphide of arsenic, boil the potassia solution of the sulphide of arsenic under examination with hydrate of teroxide of bismuth, filter off from the tersulphide of bismuth formed, and test the filtrate for arsenious and arsenic acids. If silver is to be used as the reagent to distinguish between the two acids in the filtrate, the sulphide of arsenic may also be dissolved in ammonia, the solution mixed with nitrate of silver, the fluid filtered off from the sulphide of silver formed, and the filtrate cautiously tested with dilute nitric acid, to see whether a yellow or a brown precipitate or a mixture of both is produced.

§ 134.

SUPPLEMENT TO THE SIXTH GROUP.

Molybdic Acid ($Mo\,O_3$).

Molybdenum is silvery-white, the protoxide of the metal ($Mo\,O$) is black, the binoxide ($Mo\,O_2$) dark brown. The metal and the two oxides, when heated in the air, oxidize to molybdic acid ($Mo\,O_3$). Molybdic acid is a white, porous mass, which in water separates as fine scales; it fuses at a red-heat; in close vessels it volatilizes only at a very high temperature, in the air easily at a red-heat, subliming to transparent laminæ and needles. The non-ignited acid dissolves in acids. The solutions are colorless; in contact with zinc or tin they first turn blue, then green, and ultimately black, with separation of protoxide of molybdenum; when digested with copper, they acquire a red tint, in consequence of ensuing reduction of the acid to binoxide. Ferrocyanide of potassium produces a reddish-brown precipitate, infusion of galls a green precipitate. Hydrosulphuric acid, when added in small proportion, imparts a blue tint to solutions of molybdic acid; when added in larger proportion, it produces a brownish-black precipitate; the fluid over the latter at first appears green, but after standing some time, and upon application of heat, it deposits an additional portion of brownish-black tersulphide of molybdenum ($Mo\,S_3$). The precipitated tersulphide

of molybdenum dissolves in sulphides of the alkali metals; acids reprecipitate from the sulphur salts the sulphur acid ($Mo S_3$). When roasted at a red-heat in the air or heated with nitric acid, sulphide of molybdenum is converted into molybdic acid.

Molybdic acid dissolves readily in solutions of pure alkalies and carbonates of the alkalies; from rather concentrated solutions, sulphuric, nitric, and hydrochloric acids throw down molybdic acid, which redissolves upon further addition of the precipitant. The solutions of molybdates of the alkalies are colored yellow by hydrosulphuric acid, and give afterwards, upon addition of acids, a brownish-black precipitate. For the deportment of molybdic acid with phosphoric acid and ammonia, see § 143, 11.

B.—Deportment of the Acids and their Radicals with Reagents.

§ 135.

The reagents which serve for the detection of the acids are divided, like those used for the detection of the bases, into GENERAL REAGENTS, *i. e.*, such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, *i.e.*, such as serve to effect the detection and identification of the INDIVIDUAL ACIDS. The groups into which we classify the various acids can scarcely be defined and limited with the same degree of precision as those into which the bases are divided.

The two principal groups into which acids are divided are those of INORGANIC and ORGANIC ACIDS. We base this division upon those characteristics by which, irrespectively of theoretical considerations, the ends of analysis are most easily attained. We select therefore here, as the characteristic mark to guide us in the classification into organic and inorganic acids, the deportment which the various acids manifest at a high temperature, and call *organic* those acids of which the salts—(particularly those which have an alkali or an alkaline earth for base)—are decomposed upon ignition, the decomposition being attended with separation of carbon.

By selecting this deportment at a high temperature as the distinctive characteristic of organic acids, we are enabled to determine at once by a most simple preliminary experiment the class to which an acid belongs. The salts of organic acids with alkalies or alkaline earths are converted into carbonates when heated to redness.

Before proceeding to the special study of the several acids considered in this work, I give here, the same as I have done with the bases, a general view of the whole of them classified in groups.

§ 136.

CLASSIFICATION OF ACIDS IN GROUPS.

I. Inorganic Acids.

FIRST GROUP:

Division *a.* *Arsenious acid, arsenic acid, chromic acid* (selenious acid, sulphurous and hyposulphurous acids, iodic acid).

Division *b.* *Sulphuric acid* (hydrofluosilicic acid).

Division *c.* *Phosphoric acid, boracic acid, oxalic acid, hydrofluoric acid.*

Division *d. Carbonic acid, silicic acid.*

SECOND GROUP:

Chlorine and *hydrochloric acid*, *bromine* and *hydrobromic acid*, *iodine* and *hydriodic acid*, *cyanogen* and *hydrocyanic acid*, together with *hydroferro-* and *hydroferricyanic acids*, *sulphur* and *hydrosulphuric acid* (nitrous acid and hypochlorous acid).

THIRD GROUP:

Nitric acid, chloric acid.

II. ORGANIC ACIDS.

FIRST GROUP:

Oxalic acid, tartaric acid, citric acid, malic acid (racemic acid).

SECOND GROUP:

Succinic acid, benzoic acid.

THIRD GROUP:

Acetic acid, formic acid.

I. INORGANIC ACIDS.

§ 137.

First Group.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY CHLORIDE OF BARIUM.

This group is again subdivided into four divisions, viz.:

1. Acids which are decomposed in acid solution by hydrosulphuric acid, and to which attention has therefore been directed already in the testing for bases, viz., ARSENIOUS ACID, ARSENIC ACID, and CHROMIC ACID. (In a supplement, page 129, I give selenious acid, sulphurous acid, and hyposulphurous acid, the latter because it is decomposed and detected by the mere addition of hydrochloric acid to the solution of one of its salts; and also iodic acid.)
2. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta compounds of which are insoluble in hydrochloric acid. Of the acids claiming our attention here, SULPHURIC ACID alone belongs to this class. (In a supplement, page 132, I give hydrofluosilic acid.)
3. Acids which are not decomposed in an acid solution by hydrosulphuric acid, and the baryta compounds of which dissolve in hydrochloric acid, apparently WITHOUT DECOMPOSITION, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation; these are PHOSPHORIC ACID, BORACIC ACID, OXALIC ACID, and HYDROFLUORIC ACID. (Oxalic acid belongs more properly to the organic group. We consider it, however, here with the acids of the inorganic class, as the property of its salts to be decomposed upon ignition without actual carbonization may lead to its being overlooked as an organic acid.)
4. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta salts of which are soluble in hydrochloric acid, WITH DECOMPOSITION (separation of the acid): CARBONIC ACID, SILICIC ACID.

First Division of the First Group of the Inorganic Acids.

§ 138.

a. ARSENIOUS ACID and ARSENIC ACID are, as we have seen above, decomposed by hydrosulphuric acid, and are precipitated by that reagent respectively as ter- and pentasulphide of arsenic. As this would lead to confounding them rather with the metallic oxides than with other acids, it has been deemed more judicious to class these two acids with the oxides of the sixth group. (See § 131 and § 132.)

b. CHROMIC ACID ($Cr\,O_3$).

1. Chromic acid presents the appearance of a scarlet-red crystalline mass, or of distinct acicular crystals. Upon ignition it is resolved into sesquioxide of chromium and oxygen. It deliquesces rapidly upon exposure to the air. It dissolves in water, imparting to the fluid a deep reddish-brown tint, which remains still visible in very dilute solutions.

2. The chromates are all red or yellow, and for the most part insoluble in water. Part of them are decomposed upon ignition; those with alkaline bases are fixed, and soluble in water; the solutions of the neutral alkaline chromates are yellow, those of the alkaline bichromates are red. These tints are still visible in highly dilute solutions. The yellow color of the solution of a neutral salt changes to red on the addition of a mineral acid, owing to the formation of an acid chromate.

3. *Hydrosulphuric acid* reduces chromic acid readily when present in the solution in the free state, more difficultly when present in form of a chromate; sesquioxide of chromium, water, and sulphuric acid are formed in this process, and sulphur precipitates. Heat promotes this decomposition. If no free acid is present, a greenish-gray precipitate is produced, consisting of a mixture of hydrated sesquioxide of chromium and sulphur. But if free acid is present, the precipitate is far less considerable, and consists of pure sulphur. In the latter case, the salt of sesquioxide of chromium formed imparts a green tint to the fluid, which may lead to the erroneous impression that the precipitate itself is green.

4. Chromic acid may also be reduced to sesquioxide of chromium by means of many other substances, and more particularly by *sulphurous acid*, or by heating with *hydrochloric acid*, especially upon the addition of alcohol (in which case chloride of ethyle and aldehyde are evolved); also by *metallic zinc*, or by heating with *tartaric acid*, *oxalic acid*, &c. All these reactions are clearly characterized by the change of the red or yellow color of the solution to the green tint of the salt of sesquioxide of chromium.

5. *Chloride of barium* produces a yellowish-white precipitate of CHROMATE OF BARYTA ($Ba\,O, Cr\,O_3$), which is soluble in dilute hydrochloric acid and nitric acid.

6. *Nitrate of silver* produces a dark purple-red precipitate of CHROMATE OF SILVER ($Ag\,O, Cr\,O_3$), which is soluble in nitric acid and in ammonia; in acid solutions it produces a precipitate of BICHROMATE OF SILVER ($Ag\,O, 2\,Cr\,O_3$).

7. *Acetate of lead* produces a yellow precipitate of CHROMATE OF LEAD ($Pb\,O, Cr\,O_3$), which is soluble in potassa, but only difficultly soluble in

dilute nitric acid. Upon heating with alkalies, the yellow neutral salt is converted into basic red chromate of lead ($2 PbO, CrO_3$).

8. If insoluble chromates are fused together with *carbonate of soda* and *nitrate of soda*, and the fused mass is treated with water, the fluid produced appears YELLOW from the alkaline chromate which it holds in solution; upon the addition of an acid the yellow color changes to red. The oxides remain behind either in the pure state or as carbonates, if they are not soluble in the caustic soda formed from the nitrate.

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§ 139.

Remarks.—When testing for bases, we always find the chromic acid as sesquioxide of chromium, since hydrosulphuric acid reduces it to that state. The characteristic color of the solution frequently renders the application of any further test unnecessary. The reactions with salts of silver and salts of lead afford positive and confirmatory proof of the presence of chromic acid in aqueous solutions. Acid solutions are boiled with carbonate of soda in excess, and filtered; the filtrate is acidified with acetic acid, and acetate of lead then added to it. If there is reason to suppose that chromic acid is present in a solution, metallic oxides being also present, it is preferable to effect the reduction of the chromic acid by means of hydrochloric acid and alcohol, or by sulphurous acid, instead of reducing it by hydrosulphuric acid.

§ 140.

Supplement to the First Division of the First Group.

a. Selenious acid (SeO_2). Sublimed anhydrous selenious acid appears in form of white four-sided needles, its hydrate in form of crystals resembling those of nitrate of potassa. Both the acid and its hydrate dissolve readily in water to a strongly acid fluid. Of the neutral salts only those with the alkalies are soluble in water. All selenites dissolve readily in nitric acid, with the exception of the selenites of lead and silver, which dissolve with difficulty. Hydrochloric acid, even when boiling, fails to decompose selenites; sulphuric acid decomposes them readily with the aid of heat. *Hydrosulphuric acid* produces in solutions of selenious acid or of selenites (in presence of free hydrochloric acid) a yellow precipitate of SULPHIDE OF SELENIUM, which, upon heating, turns reddish-yellow, and is soluble in sulphide of ammonium. *Chloride of barium* produces (after neutralization of the free acid, should any be present) a white precipitate of *selenite of baryta*, which is soluble in hydrochloric acid and in nitric acid. *Protochloride of tin* produces a red precipitate of SELENIUM, which turns gray at a high temperature; *sulphurous acid* produces the same precipitate. When exposed on a charcoal support to the *reducing flame*, the selenites evolve selenium, exhaling at the same time a characteristic odor of decaying horse-radish.

b. Sulphurous acid (SO_2) is a colorless, uninflammable gas, which exhales the stifling odor of burning sulphur. It dissolves copiously in water. The solution has the odor of the gas, reddens litmus paper, and bleaches Brazil-wood paper. It absorbs oxygen from the air, and is

thereby converted into sulphuric acid. The salts of sulphurous acid are colorless. Of the neutral sulphites those with alkaline base only are readily soluble in water; many of the sulphites insoluble or difficultly soluble in water dissolve in an aqueous solution of sulphurous acid, but fall down again upon boiling. All the sulphites evolve sulphurous acid when treated with *sulphuric acid* or *hydrochloric acid*. *Chlorine water* dissolves most sulphites to sulphates. *Chloride of barium* precipitates neutral sulphites, but not free sulphurous acid. The precipitate dissolves in hydrochloric acid. *Hydrosulphuric acid* decomposes free sulphurous acid, water being formed and free sulphur eliminated, which latter separates from the fluid. If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from *zinc* and *hydrochloric acid*, hydrosulphuric acid is immediately evolved along with the hydrogen, and the gas now produces a black coloration or a black precipitate in a solution of acetate of lead to which has been added a sufficient quantity of solution of soda to redissolve the precipitate which forms at first. Sulphurous acid is a powerful reducing agent; it reduces chromic acid, permanganic acid, chloride of mercury (to subchloride), decolorizes iodide of starch, produces a blue precipitate in a mixture of ferricyanide of potassium and sesquichloride of iron, &c. With a hydrochloric acid solution of *protochloride of tin*, a brown precipitate of PROTOSULPHIDE OF TIN is formed after some time.

c. Hyposulphurous acid ($S_2 O_2$). This acid does not exist in the free state. Its salts are generally soluble in water. The solutions of most hyposulphites may be boiled without suffering decomposition; hyposulphite of lime is resolved upon boiling into sulphite of lime and sulphur. If *hydrochloric acid* or *sulphuric acid* is added to the solution of a hyposulphite, the fluid remains at first clear and inodorous, but after a short time—the shorter the more concentrated the solution—it becomes more and more turbid, owing to the separation of sulphur, and exhales the odor of sulphurous acid. Application of heat promotes this decomposition. *Nitrate of silver* produces a white precipitate of HYPOSULPHITE OF SILVER, which is soluble in an excess of the hyposulphite; after a little while (upon heating almost immediately) the precipitate turns black, being decomposed into sulphide of silver and sulphuric acid. Hyposulphite of soda dissolves chloride of silver; upon the addition of an acid the solution remains clear at first, but shortly, and upon boiling, immediately, sulphide of silver separates. *Chloride of barium* produces a white precipitate, which is soluble in much water, more especially hot water, and is decomposed by hydrochloric acid.

d. Iodic acid ($I O_5$). Iodic acid crystallizes in white, six-sided tables; at a moderate heat it is resolved into iodine vapor and oxygen; it is readily soluble in water. The salts are decomposed upon ignition, being resolved either into oxygen and a metallic iodide, or into iodine, oxygen, and metallic oxide; the iodates with an alkaline base alone dissolve readily in water. *Chloride of barium* throws down from solution of iodates of the alkalies a white precipitate of IODATE OF BARYTA, which is soluble in nitric acid; *nitrate of silver*, a white, granular-crystalline precipitate of IODATE OF SILVER, which dissolves readily in ammonia, but only sparingly in nitric acid. *Hydrosulphuric acid* throws down from solutions of iodic acid and iodates IODINE, which then dissolves in hydriodic acid; if an excess of hydrosulphuric acid is added, the fluid loses its color, and sulphur separates, the iodine being converted into hydriodic acid. *Sul-*

phurous acid throws down IODINE, which upon addition of an excess of the acid is converted into hydriodic acid.

Second Division of the First Group of the Inorganic Acids.

§ 141.

SULPHURIC ACID ($S O_3$).

1. Anhydrous sulphuric acid is a white, feathery-crystalline mass, which emits strong fumes upon exposure to the air; hydrated sulphuric acid forms an oily liquid, colorless and transparent like water. Both the anhydrous and hydrated acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydrous acid, with a hissing noise.

2. Most of the sulphates are soluble in water; the insoluble sulphates are generally white; the soluble sulphates, in the crystalline state, are for the most part colorless. The sulphates of the alkalies and alkaline earths are not decomposed upon ignition.

3. *Chloride of barium* produces even in exceedingly dilute solutions of sulphuric acid and of the sulphates a finely-pulverulent, heavy, white precipitate of SULPHATE OF BARYTA ($Ba O, S O_3$), which is insoluble in hydrochloric acid and in nitric acid. From very dilute solutions the precipitate separates only after standing some time. In presence of the citrate of an alkali, the precipitate forms only after addition of hydrochloric acid (*Spiller*).

4. *Acetate of lead* produces a heavy, white precipitate of SULPHATE OF LEAD ($Pb O, S O_3$) which is sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid.

5. The salts of sulphuric acid with the alkaline earths which are insoluble in water and acids are converted into CARBONATES, by fusion with *alkaline carbonates.* But the sulphate of lead is reduced to the state of PURE OXIDE when treated in this manner. Both the conversion of the former into carbonates, and the reduction of the latter to the state of oxide, are attended with the formation of an alkaline sulphate. The sulphates of the alkaline earths and sulphate of lead, are also resolved into insoluble carbonates and soluble alkaline sulphate when boiled with concentrated solutions of carbonates of the alkalies.

6. Upon fusing sulphates with *carbonate of soda* on charcoal in the inner flame of the blowpipe, the sulphuric acid is reduced, and sulphide of sodium formed, which may be readily recognised by the odor of hydrosulphuric acid emitted upon moistening the sample and the part of the charcoal into which the fused mass has penetrated, and adding some acid. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and then moistened with water and some acid, a black stain of sulphide of silver is immediately formed.

Remarks.—The characteristic and exceedingly delicate reaction of sulphuric acid with salts of baryta renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with sulphate of baryta, precipitates of chloride of barium, and particularly of nitrate of baryta, which are formed upon

mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of baryta, since they redissolve immediately upon diluting the acid fluid with water. To detect free sulphuric acid in presence of a sulphate, the fluid under examination is mixed with a very little cane-sugar, and the mixture evaporated to dryness in a porcelain dish at 212° Fah. If free sulphuric acid was present, a black residue remains, or, in the case of most minute quantities, a blackish-green residue. Other free acids do not decompose cane-sugar in this way (*Runge*).

§ 142.

Supplement to the Second Division of the First Group.

HYDROFLUOSILICIC ACID ($H F, Si F_2$).

Hydrofluosilicic acid is a very acid fluid; when evaporated on platinum, it volatilizes completely as fluoride of silicon and hydrofluoric acid. When evaporated on glass, it etches the latter. With bases it forms water and silico-fluorides of the metals, which are most of them soluble in water, redden litmus paper, and are resolved upon ignition into metallic fluorides and fluoride of silicon.

Chloride of barium forms a crystalline precipitate with hydrofluosilicic acid (§ 94, 6). Chloride of strontium and acetate of lead form no precipitates with this acid; *salts of potassa* precipitate transparent GELATINOUS SILICO-FLUORIDE OF POTASSIUM; *ammonia* in excess precipitates HYDRATED SILICIC ACID, with formation of fluoride of ammonium. When metallic silico-fluorides are heated with concentrated *sulphuric acid* in a platinum vessel covered with glass, the glass is ETCHED (§ 147, 5).

Third Division of the First Group of the Inorganic Acids.

§ 143.

a. PHOSPHORIC ACID ($P O_5$).

1. Phosphorus is a colorless, transparent, solid body, of 2·089 specific gravity; it has a waxy appearance. Taken internally, it acts as a virulent poison. It fuses at 113°, and boils at 554° Fah. By the influence of light, phosphorus kept under water turns first yellow, then red, and is finally covered with a white crust. If phosphorus is exposed to the air, at the common temperature, it exhales a garlic odor, shines in the dark, and emits fumes of phosphorous acid, into which substance it is gradually entirely converted. Phosphorus very readily takes fire spontaneously, and burns with a luminous flame, being converted into phosphoric acid, which is dissipated for the most part in white fumes through the surrounding air. Nitric acid and nitrohydrochloric acid dissolve phosphorus pretty readily upon heating. The solutions contain at first, besides phosphoric acid, also phosphorous acid. Hydrochloric acid does not dissolve phosphorus; if phosphorus is boiled with solution of soda or potassa, or with milk of lime, hypophosphites and phosphates are formed, whilst spontaneously inflammable phosphuretted hydrogen gas escapes. If a trace of phosphorus is put into a hydrogen gas-evolution apparatus supplied with pure zinc and pure dilute sulphuric acid, phosphide of hydrogen is evolved with the hydrogen, and the gas burns now with

a conical, emerald-green flame, surrounded by an outer hardly visible pale blue mantle. The color does not lose in intensity upon transmitting the gaseous mixture over hydrate of potassa or caustic lime, which should always be done, in order to remove any hydrosulphuric acid that may be evolved along with the other two gases. If the gas is not kindled, it shines in the dark. If it is received under water, it will form white fumes when it comes in contact with the air (*Dusart*). For the deportment of phosphoric acid upon boiling with dilute sulphuric acid in a distilling apparatus, see § 225.

2. Anhydrous phosphoric acid is a white, snowlike mass, which rapidly deliquesces in the air, and dissolves in water with a hissing noise. It forms with water and bases three different series of compounds: viz., with three equivalents of water or base, hydrate of common phosphoric acid or common phosphates; with two equivalents of water or base, hydrate of pyrophosphoric acid or pyrophosphates; with one equivalent of water or base, hydrate of metaphosphoric acid or metaphosphates.

The phosphates which we generally meet with in nature and in analytical investigations belong, as a rule, to the tribasic series; we therefore make them alone the object of a fuller study in this place, devoting a supplemental paragraph to a briefer consideration of monobasic and bibasic phosphoric acids, and their salts.

3. The hydrate of common phosphoric acid ($3\,HO, PO_5$) forms colorless and pellucid crystals, which deliquesce rapidly in the air to a syrupy non-caustic liquid. The action of heat changes it into hydrated pyro- or metaphosphoric acid, according as either one or two equivalents of water are expelled. Heated in an open platinum dish, the hydrate of common phosphoric acid, if pure, volatilizes completely, though with difficulty, in white fumes.

4. The action of heat fails to decompose the tribasic phosphates with fixed bases, but converts them into pyrophosphates, if they contain one equivalent of basic water or ammonia, and into metaphosphates, if they contain two equivalents. The tribasic phosphates with alkaline base alone are soluble in water, in the neutral state. The solutions manifest an alkaline reaction. If pyro- or metaphosphates are fused with carbonate of soda, the fused mass contains the phosphoric acid invariably in the tribasic state.

5. *Chloride of barium* produces in aqueous solutions of the neutral or basic phosphates, but not in solution of the hydrate, a white precipitate of PHOSPHATE OF BARYTA [$2\,BaO, HO, PO_5$; or $3\,BaO, PO_5$],* which is soluble in hydrochloric acid and in nitric acid, but difficultly soluble in chloride of ammonium.

6. *Solution of sulphate of lime* produces in neutral or alkaline solutions of phosphates, but not in solutions of the hydrate, a white precipitate of PHOSPHATE OF LIME ($2\,CaO, HO, PO_5$ or $3\,CaO, PO_5$) which dissolves readily in acids, even in acetic acid, but with difficulty in chloride of ammonium.

7. *Sulphate of magnesia* produces in concentrated neutral solutions of phosphates a white precipitate of PHOSPHATE OF MAGNESIA ($2\,MgO, HO, PO_5 + 14\,aq.$), which often separates only after some time; upon

* Precipitates of the former composition are produced in solutions containing an alkaline phosphate with two equivalents of a fixed base or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate with three equivalents of a fixed base or ammonia.

boiling, however, a precipitate of basic salt ($3\ MgO, PO_5 + 5\ aq.$) is thrown down immediately. The latter precipitate forms also upon addition of sulphate of magnesia to the solution of a basic alkaline phosphate. But if *sulphate of magnesia*, mixed with a sufficient quantity of chloride of ammonium to leave the solution clear upon addition of ammonia, is added to a solution of free phosphoric acid or of an alkaline phosphate, and ammonia in excess is then added, a white, crystalline, and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\ MgO, NH_4O, PO_5 + 12\ aq.$) is formed, even in highly dilute solutions. This precipitate is insoluble in ammonia and most sparingly soluble in chloride of ammonium, but dissolves readily in acids, even in acetic acid. It makes its appearance often only after the lapse of some time; stirring promotes its separation (see § 97, 7).

8. *Nitrate of silver* throws down from solutions of neutral and basic alkaline phosphates a light-yellow precipitate of PHOSPHATE OF SILVER ($3\ AgO, PO_5$), which is readily soluble in nitric acid and in ammonia. If the solution contained a basic phosphate, the fluid in which the precipitate is suspended manifests a neutral reaction; whilst the reaction is acid if the solution contained a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives for the 3 equivalents of oxide of silver which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water; and as the latter does not neutralize the acid properties of the nitric acid, the solution becomes acid.

9. *Acetate of lead* produces in neutral and alkaline solutions of phosphates a white precipitate of PHOSPHATE OF LEAD ($3\ PbO, PO_5$), which is readily soluble in nitric acid, but nearly insoluble in acetic acid. It fuses before the blowpipe; the cold beads exhibit brilliant facets.

10. If to a solution containing phosphoric acid and the *least possible excess* of hydrochloric or nitric acid, a tolerably large amount of acetate of soda is added, and then a drop of *sesquichloride of iron*, a yellowish-white, flocculent-gelatinous precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON ($Fe_2O_3, PO_5 + 4\ aq.$) is formed. An excess of sesquichloride of iron must be avoided, as acetate of sesquioxide of iron (of red color) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths; to effect the complete separation of the phosphoric acid from the alkaline earths, a sufficient quantity of sesquichloride of iron is added to impart a reddish color to the solution, which is then boiled (whereby the whole of the sesquioxide of iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of sesquioxide of iron, boil the hydrochloric acid solution with sulphite of soda until the sesquichloride is reduced to protochloride, which reduction is indicated by the decoloration of the solution; add carbonate of soda until the fluid is nearly neutral, then acetate of soda, and finally one drop of sesquichloride of iron. The reason for this proceeding is, that acetate of protoxide of iron does not dissolve phosphate of sesquioxide of iron.

11. If some *molybdate of ammonia* is mixed in a test-tube with hydrochloric acid or nitric acid in sufficient quantity to redissolve the precipitate which first forms, and a little of a fluid containing phos-

phoric acid is then added, the fluid acquires a yellow color, and after some time a yellow precipitate separates, which, in presence of molybdic acid in excess, is insoluble in acids, and contains MOLYBDIC ACID, AMMONIA, AND A LITTLE PHOSPHORIC ACID. Application of heat greatly promotes the reaction. This reaction is so delicate, that the phosphoric acid may be detected by its means in almost all salts and most minerals containing it. As the yellow compound is decomposed by free phosphoric acid, an excess of the fluid containing the phosphoric acid must be carefully avoided. The yellow precipitate may, when it has subsided, be perceived even in dark-colored fluids (*Svanberg* and *Struve*). By washing it with a solution of molybdate of ammonia, supersaturated with hydrochloric acid, dissolving in ammonia, and adding a mixture of sulphate of magnesia, chloride of ammonium, and ammonia, phosphate of magnesia and ammonia is produced.

12. If a finely powdered substance containing phosphoric acid (or also a metallic phosphide) is intimately mixed with 5 parts of a flux consisting of 3 parts of carbonate of soda, 1 part of nitrate of potassa, and 1 part of silicic acid, the mixture fused in a platinum spoon or crucible, the fused mass boiled with water, the solution obtained decanted, carbonate of ammonia added to it, the fluid boiled again, and the silicic acid which is thereby precipitated filtered off, the filtrate now holds in solution alkaline phosphate, and may accordingly be tested for phosphoric acid as directed in 11, or in some other way.

13. *White of egg* is not precipitated by solution of hydrate of tribasic phosphoric acid, nor by solutions of tribasic phosphates, mixed with acetic acid.

§ 144.

Supplement.

a. Bibasic phosphoric acid. The solution of the hydrate $2\,HO, PO_5$ is converted by boiling into solution of the hydrate $3\,HO, PO_5$. The solutions of the salts bear heating without suffering decomposition; but upon boiling with a strong acid, the phosphoric acid is converted into the tribasic state. If the salts are fused with carbonate of soda in excess, tribasic phosphates are produced. Of the neutral pyrophosphates only those with alkaline bases are soluble in water; the acid salts (*e. g.*, NaO, HO, PO_5) are by ignition converted into metaphosphates (NaO, PO_5). *Chloride of barium* fails to precipitate the free acid; from solutions of the salts it precipitates PYROPHOSPHATE OF BARYTA ($2\,BaO, PO_5$). *Nitrate of silver* throws down from a solution of the hydrate, especially upon addition of an alkali, a white, earthy-looking precipitate of PYROPHOSPHATE OF SILVER ($2\,AgO, PO_5$), which is soluble in nitric acid and in ammonia. *Sulphate of magnesia* precipitates PYROPHOSPHATE OF MAGNESIA ($2\,MgO, PO_5$). The precipitate dissolves in an excess of the phosphate, as well as in an excess of the sulphate of magnesia. Ammonia fails to precipitate it from these solutions. Upon boiling the solution, it separates again. *White of egg* is not precipitated by solution of the hydrate, nor by solutions of the salts, mixed with acetic acid. *Molybdate of ammonia*, with addition of hydrochloric acid, fails to produce a precipitate.

β. Monobasic phosphoric acid. Five sorts of monobasic phosphates are known, and the hydrates also of most of these have been produced.

The several reactions by which to distinguish between these I will not enter upon here, and confine myself to the simple observation that the monobasic phosphoric acids differ from the bibasic and tribasic phosphoric acids in this, that the solutions of the hydrates of the monobasic acids precipitate *white of egg* at once, and the solutions of their salts, after addition of acetic acid. Those hydrates and salts which are precipitated by *nitrate of silver* produce with that reagent a white precipitate. A mixture of *sulphate of magnesia*, chloride of ammonium, and ammonia fails to precipitate the monobasic phosphoric acids and their salts, or produces precipitates soluble in chloride of ammonium. All monobasic phosphates yield upon fusion with carbonate of soda tribasic phosphate of soda.

§ 145.

b. Boracic Acid ($B\,O_3$).

1. Boracic acid, in the anhydrous state, is a colorless, fixed glass, fusible at a red heat; hydrate of boracic acid ($3\,H\,O,\ 2\,B\,O_3$) is a porous, white mass; in the crystalline state ($3\,H\,O,\ 2\,B\,O_3 + 3$ aq.), it presents small scaly laminæ. It is soluble in water and in spirit of wine; upon evaporating the solutions, a large proportion of boracic acid volatilizes along with the aqueous and alcoholic vapors. The solutions redden litmus paper, and impart to turmeric paper a faint brown-red tint, which acquires intensity upon drying. The borates are not decomposed upon ignition; those with alkaline bases alone are readily soluble in water. The solutions are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, if not too highly dilute, a white precipitate of BORATE OF BARYTA, which is soluble in acids and ammoniacal salts. The formula of this precipitate, when thrown down from solutions of neutral borates, is $Ba\,O,\ B\,O_3$ + aq.; when thrown down from solutions of acid borates, $3\,Ba\,O,\ 5\,B\,O_3 + 6$ aq. (*H. Rose*).

3. *Nitrate of silver* produces in concentrated solutions of neutral borates of the alkalies a white precipitate, inclining slightly to yellow from admixture of free oxide of silver ($Ag\,O,\ B\,O_3 + H\,O$); in concentrated solutions of acid borates, a white precipitate of $3\,Ag\,O,\ 4\,B\,O_3$. Dilute solutions of borates give with nitrate of silver a grayish-brown precipitate of oxide of silver (*H. Rose*). All these precipitates dissolve in nitric acid and in ammonia.

4. If *sulphuric acid* or *hydrochloric acid* is added to highly concentrated, hot prepared solutions of alkaline borates, the BORACIC ACID separates upon cooling, in the form of shining crystalline scales.

5. If alcohol is poured over free boracic acid or a borate—with addition, in the latter case, of *a sufficient quantity of concentrated sulphuric acid* to liberate the boracic acid—and the alcohol is kindled, the flame appears of a very distinct YELLOWISH-GREEN color, especially upon stirring the mixture; this tint is imparted to the flame by the ignited boracic acid which volatilizes with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, kindling the alcohol, allowing it to burn for a short time, then extinguishing the flame, and afterwards rekindling it. At the first flickering of the flame its borders will now appear green, even though

the quantity of the boracic acid be so minute that it fails to produce a perceptible coloring of the flame, when treated in the usual manner. As salts of copper also impart a green tint to the flame of alcohol, the copper which might be present must first be removed by means of hydrosulphuric acid. Presence of metallic chlorides also may lead to mistakes, as the chloride of ethyle formed in that case colors the borders of the flame greenish.

6. If the solution of a borate is mixed with hydrochloric acid to slight, but distinct, acid reaction, and a slip of turmeric paper is half dipped into it, and then dried on a watch-glass at 212° Fah., the dipped half shows a brown-red tint (*H. Rose*).

This reaction is very delicate; care must be taken not to confound the characteristic brownish-red coloration with the blackish-brown color which turmeric paper acquires when moistened with rather concentrated hydrochloric acid, and then dried.

7. If a substance containing boracic acid is reduced to a fine powder, this, with addition of a drop of water, mixed with a flux composed of $4\frac{1}{2}$ parts of bisulphate of potassa and 1 part of finely pulverized fluoride of calcium, free from boracic acid, and the paste exposed on the loop of a platinum wire to the inner flame of the blowpipe, fluoride of boron escapes, which imparts to the flame—though only for a few instants—a yellow-green tint (*Turner*).

§ 146.

c. Oxalic Acid ($C_2\ O_3 = \bar{O}$).

1. The hydrate of oxalic acid ($H\ O, C_2\ O_3$) is a white powder; the crystallized acid ($H\ O, C_2\ O_3 + 2$ aq.) forms colorless rhombic prisms. Both dissolve readily in water and in spirit of wine. When heated rapidly in open vessels, part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating and provoke coughing. If the hydrate is heated in a test-tube, the greater part of it sublimes unaltered.

2. The whole of the oxalates undergo decomposition at a red heat, the oxalic acid being converted into carbonic acid and carbonic oxide. Those with an alkali or an alkaline earth for base are in this process converted into carbonates (if pure, almost without separation of charcoal); those with a metallic base leave either the pure metal or the oxide behind, according to the greater or less degree of reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. *Chloride of barium* produces in neutral solutions of oxalates a white precipitate of OXALATE OF BARYTA ($Ba\ O, \bar{O} +$ aq.), which is soluble in nitric acid and in hydrochloric acid, but dissolves more sparingly in ammoniacal salts than borate of baryta.

4. *Nitrate of silver* produces in neutral solutions of oxalates a white precipitate of OXALATE OF SILVER ($Ag\ O, \bar{O}$), which is soluble in nitric acid and in ammonia.

5. *Lime-water* and all the *soluble salts of lime*, and consequently also *solution of sulphate of lime*, produce in even highly dilute solutions of free oxalic acid or of oxalates, white, finely pulverulent precipitates of

OXALATE OF LIME (CaO, O), which dissolve readily in hydrochloric acid and in nitric acid, but are nearly insoluble in oxalic acid and in acetic acid. The presence of salts of ammonia does not interfere with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of the free oxalic acid by salts of lime. In *highly dilute* solutions the precipitate is only formed after some time.

6. If hydrated oxalic acid (or an oxalate), in the dry state, is heated with an excess of *concentrated sulphuric acid*, the latter withdraws from the oxalic acid its constitutional water, and thus causes its decomposition into CARBONIC ACID and CARBONIC OXIDE ($C_2O_3 = CO + CO_2$), the two gases escaping with effervescence. If the quantity operated upon is not too minute, the escaping carbonic oxide gas may be kindled; it burns with a blue flame. Should the sulphuric acid acquire a dark color in this reaction, this is a proof that the oxalic acid contained some organic substance in admixture.

7. If oxalic acid or an oxalate is mixed with some finely pulverized binoxide of manganese (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence ensues, caused by the escaping carbonic acid ($MnO_2 + C_2O_3 + SO_3 = MnO, SO_3 + 2CO_2$).

8. If oxalate of lime or any other insoluble oxalate is boiled with a concentrated solution of *carbonate of soda*, and the fluid filtered, the oxalic acid is obtained in the filtrate in combination with soda, whilst the precipitate contains the base as oxide or as carbonate.

§ 147.

d. HYDROFLUORIC ACID (HF).

1. Hydrofluoric acid is a colorless, highly volatile fluid of pungent odor; it emits fumes when exposed to the air, and is miscible with water in all proportions. Hydrofluoric acid is distinguished from all other acids by the exclusive property it possesses of dissolving crystallized silicic acid, and also the silicates which are insoluble in hydrochloric acid. Fluoride of silicon and water are formed in the process of solution ($2HF + Si.O_2 = SiF_2 + 2HO$). Hydrofluoric acid decomposes with metallic oxides in the same manner, metallic fluorides and water being formed.

2. The fluorides of the alkali metals are soluble in water; the solutions have an alkaline reaction. The fluorides of the metals of the alkaline earths are either altogether insoluble in water, or they dissolve in that menstruum only with very great difficulty. Fluoride of aluminium is readily soluble. Most of the fluorides corresponding to the oxides of the heavy metals are very difficultly soluble in water, for instance, fluorides of copper, lead, and zinc; many other of the fluorides of the heavy metals dissolve in water without difficulty, as, for instance, the sesquifluoride of iron, protofluoride of tin, fluoride of mercury, &c. Many of the fluorides insoluble or difficultly soluble in water dissolve in free hydrofluoric acid, others do not. Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Chloride of barium* precipitates free hydrofluoric acid incompletely, but upon addition of ammonia a copious, white precipitate of FLUORIDE OF BARIUM (BaF) forms immediately, which is soluble in hydrochloric acid, and not insoluble in chloride of ammonium.

4. *Chloride of calcium* produces in aqueous solutions of hydrofluoric acid or of fluorides a gelatinous precipitate of FLUORIDE OF CALCIUM (Ca F), which is so transparent, as at first to induce the belief that the fluid has remained perfectly bright. Addition of ammonia promotes the complete separation of the precipitate. The precipitated fluoride of calcium is very slightly soluble in hydrochloric acid and nitric acid in the cold; it dissolves somewhat more largely upon boiling with hydrochloric acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the salt of ammonia formed retains it in solution. It is scarcely more soluble in free hydrofluoric acid than in water. It is insoluble in alkaline fluids.

5. If a finely pulverized fluoride, no matter whether soluble or insoluble, is treated in a platinum crucible with *concentrated sulphuric acid*, the crucible covered with the convex face of a watch-glass coated with bees-wax, which has been removed again in some places by tracing lines in it with a pointed instrument,* the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found etched into the glass. If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This reappearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess.

This reaction (5) fails if there is too much silicic acid present, or if the body under examination is not decomposed by sulphuric acid. In such cases the one or the other of the two following methods is resorted to, according to circumstances.

6. If we have to deal with a fluoride *decomposable by sulphuric acid*, but mixed with a large proportion of silicic acid, the fluorine in it may be detected by heating the mixture in a test-tube with *concentrated sulphuric acid*, as FLUOSILICIC GAS is evolved in this process, which forms dense white fumes in moist air. If the gas is conducted into water, through a bent tube moistened inside, the latter has its transparency more or less impaired, by the separation of silicic acid. If the quantity operated upon is rather considerable, hydrate of silicic acid separates in the water, and the fluid is rendered acid by hydrofluosilicic acid.

The following process answers best for the detection of smaller quantities of fluorine. Add to the substance under examination some lumps of marble (to ensure a continuous slight evolution of gas), boil the mixture in a flask with concentrated sulphuric acid, conduct the gases evolved into solution of ammonia, heat, filter, evaporate in a platinum crucible to dryness, and examine the residue by the method described in 5.—In the case of more difficultly decomposable substances bisulphate of potassa is used instead of sulphuric acid, and the mixture, to which some marble is likewise added, heated to fusion, and kept in that state for some time.

7. Compounds not decomposable by sulphuric acid must first be fused

* The coating with wax may be readily effected by heating the glass cautiously, putting a small piece of wax upon the convex face, and spreading the fused mass equally over it. The instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers best. The removal of the wax coating is effected by heating the glass gently, and wiping the wax off with a cloth.

with four parts of carbonate of soda and potassa. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel, hydrochloric acid added to feebly acid reaction, and the fluid allowed to stand until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 5. (*H. Rose.*)

8. Minute quantities of metallic fluorides in minerals, slags, &c., may also be readily detected by means of the *blowpipe*. To this end, bend a piece of platinum foil, gutter-shape, then insert it in a glass tube as shown in Fig. 29, introduce the finely triturated substance mixed with powdered phosphate of soda and ammonia fused on charcoal, and let the blowpipe flame play upon it in a manner to make the product of combustion pass into the tube. If fluorides of metals are present, hydrofluoric acid gas is evolved, which betrays its presence by its pungent odor, the dimming of the glass tube, and the yellow tint which the acid air issuing from the tube imparts to a moist slip of Brazil-wood paper* (*Berzelius, Smithson*). When silicates containing metallic fluorides are treated in this manner, gaseous fluoride of silicon is formed, which also colors yellow a moist slip of Brazil-wood paper inserted in the tube, and leads to silicic acid being deposited within the tube. After washing and drying the tube, the latter appears here and there dimmed. In the case of minerals containing water, presence of even a small proportion of metallic fluorides will, upon heating, even without addition of phosphate of soda and ammonia, usually suffice to color yellow a moistened slip of Brazil-wood paper inserted in the tube (*Berzelius*).

Fig. 29.

§ 148.

Recapitulation and remarks.—The baryta compounds of the acids of the third division are dissolved by hydrochloric acid, apparently without undergoing decomposition; alkalies therefore reprecipitate them unaltered, by neutralizing the hydrochloric acid. The baryta compounds of arsenious acid, arsenic acid, and chromic acid show, however, the same deportment; these acids must, therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from the reprecipitation of a salt of baryta by alkalies. But even leaving this point altogether out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric acid solutions the salts of baryta in question, and more particularly the borate of baryta and the fluoride of barium, if the solution contains any considerable proportion of free acid or of an ammoniacal salt. *Boracic acid* may be invariably detected by the characteristic tint which it communicates to the flame of alcohol, provided care be taken to concentrate the solution sufficiently before

* Prepared by moistening slips of fine printing-paper with decoction of Brazil-wood.

adding the alcohol, and in the case of borates, to mix the solution with a sufficient amount of concentrated sulphuric acid. Solutions of free boracic acid must be combined with an alkali before evaporating, otherwise a large portion of the acid will volatilize along with the aqueous vapors. Minute traces of boracic acid are more safely detected by the method given § 145, 6.

The detection of *phosphoric acid* in compounds soluble in water is not difficult; the reaction with sulphate of magnesia is the best adapted to effect the purpose. The detection of phosphoric acid in insoluble compounds is somewhat more difficult; but even here we have now some excellent tests, in the reaction with sesquichloride of iron and acetate of soda, and more particularly still in that with molybdate of ammonia. With regard to the former of these two tests, I repeat here once more, that a sensitive reaction is not to be expected in a fluid colored red by acetate of sesquioxide of iron, as the latter (as well as acetate of alumina) dissolves phosphate of sesquioxide of iron; the directions given in § 143, 10, must therefore be strictly attended to. As regards the reaction with molybdate of ammonia, I must not omit to remark that, on account of its extraordinary sensitiveness, the greatest possible care and caution must be observed in the application of the test; not but we may almost always or, at all events, in most cases (as arsenic acid shows the same deportment) assume the yellow color of the solution or the formation of the yellow precipitate to indicate the presence of phosphoric acid; but that the reagent used may contain a trace of phosphoric acid, very slight perhaps, yet sufficient to be brought to light by this most delicate test; the purity of the reagents used in the process must therefore always be ascertained with the greatest care, otherwise it may happen that the presence of phosphoric acid is erroneously assumed in a substance simply because one or other of the reagents employed contained a trace of that acid. It must also be borne in mind that the reaction is manifest only in presence of an *excess* of molybdic acid. If this point is lost sight of, the phosphoric acid may be readily overlooked in the very cases where it is present in the largest proportion. *Oxalic acid* may always be easily detected in aqueous solutions by solution of sulphate of lime. The formation of a finely pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt on the point, as racemic acid alone, which occurs so very rarely, gives the same reaction. In case of doubt, the oxalate of lime may be readily distinguished from the paratartrate, or racemate, by simple ignition, with exclusion of the air, as the decomposed paratartrate leaves a considerable proportion of charcoal behind; the paratartrate dissolves moreover in cold solution of potassa or soda, in which oxalate of lime is insoluble. The deportment of the oxalates with sulphuric acid, or with binoxide of manganese and sulphuric acid, affords also sufficient means to confirm the results of other tests. In insoluble salts the oxalic acid is detected most safely by decomposing the insoluble compound by boiling with solution of carbonate of soda. I must finally also call attention here to the fact that there are certain soluble oxalates which are not precipitated by salts of lime; these are more particularly oxalate of sesquioxide of chromium, and oxalate of sesquioxide of iron. Their non-precipitation is owing to the circumstance that these salts form soluble double salts with oxalate of lime. In salts decomposable by sulphuric acid, the *hydrofluoric acid* is readily detected; only, it must be borne in mind that the glass cannot be distinctly etched, if, instead of hydrofluoric

gas, fluosilicic gas alone is evolved; and therefore, in the case of compounds abounding in silica, the safer way is to try, besides the reaction given § 147, 5, also the one given in § 147, 6. In silicates which are not decomposed by sulphuric acid, the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given § 147, 7.

Fourth Division of the First Group of the Inorganic Acids.

§ 149.

a. Carbonic Acid (CO_2).

1. Carbon is a solid, tasteless, and inodorous body. The very highest degrees of heat alone can effect its fusion and volatilization (*Despretz*). Carbon is combustible, and yields carbonic acid when burnt with a sufficient supply of oxygen or atmospheric air. In the diamond the carbon is crystallized, transparent, exceedingly hard, difficultly combustible; in the form of graphite, it is opaque, blackish-gray, soft, greasy to the touch, difficultly combustible, and stains the fingers; as charcoal, produced by the decomposition (destructive distillation) of organic matters, it is black, opaque, noncrystalline—often dense, shining, difficultly combustible—often porous, dull, readily combustible.

2. Carbonic acid, at the common temperature and common atmospheric pressure, is a colorless gas of far higher specific gravity than atmospheric air, so that it may be poured from one vessel into another. It is almost inodorous, has a sourish taste, and reddens moist litmus-paper; but the red tint disappears again upon drying. Carbonic acid is readily absorbed by solution of potassa; it dissolves pretty copiously in water.

3. The aqueous solution of carbonic acid has a feebly acid, pungent taste; it transiently imparts a red tint to litmus-paper, and colors solution of litmus wine-red; it loses its carbonic acid upon the application of heat, and also when shaken with air in a half-filled bottle. Part of the carbonates lose their carbonic acid upon ignition; those with colorless oxides are white or colorless. Of the neutral carbonates, only those with alkaline bases are soluble in water. The solutions manifest a very strong alkaline reaction. Besides the carbonates with alkaline bases, those also with an alkaline earth for base, and some of those with a metallic base, dissolve as acid or bicarbonates.

4. The carbonates are decomposed by all *free acids* soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. The decomposition of the carbonates by acids is attended with EFFERVESCENCE, the carbonic acid being disengaged as a colorless and almost inodorous gas, which transiently imparts a reddish tint to litmus-paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkaline bases, since the formation of bicarbonates will frequently prevent effervescence, if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid by this method, should first be drenched with water, to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substances with the acid. If it is wished to determine by a direct experiment whether the disengaged gas is really carbonic acid or not, this may be readily accomplished by dipping the end of a glass rod in baryta-water, and inserting the rod into the test-tube,

bringing the moistened end near the surface of the fluid in the tube, when ensuing turbidity of the baryta-water on the glass rod will prove that the evolved gas is really carbonic acid, since

5. *Lime-water* and *baryta-water*, when brought into contact with carbonic acid or with soluble carbonates, produce white precipitates of neutral CARBONATE OF LIME ($Ca\,O, C\,O_2$), or neutral CARBONATE OF BARYTA ($Ba\,O, C\,O_2$). When testing for free carbonic acid, the reagents ought always to be added in excess, as the *acid* carbonates of the alkaline earths are soluble in water. The precipitated carbonates of lime and baryta dissolve in acids, with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition.

6. *Chloride of calcium* and *chloride of barium* immediately produce in solutions of neutral alkaline carbonates, precipitates of CARBONATE OF LIME or of CARBONATE OF BARYTA; in dilute solutions of bicarbonates these precipitates are formed only upon ebullition; with free carbonic acid these reagents give no precipitate.

§ 150.

b. SILICIC ACID ($Si\,O_2$).

1. Silicic acid is colorless or white, even in the hottest blowpipe flame unalterable and infusible. It fuses in the flame of the oxyhydrogen blowpipe. It is met with in two modifications (more correctly speaking, in the crystalline and in the amorphous state). It is insoluble in water and acids, with the exception of hydrofluoric acid; whilst its hydrate is soluble in acids, but only at the moment of its separation. The amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of caustic alkalies and of fixed alkaline carbonates; but the crystallized acid is insoluble or nearly so in these fluids. If either of the two is fused with pure alkalies or alkaline carbonates, a basic silicate of the alkali is obtained, which is soluble in water, and from which acids again separate hydrated silicic acid. The silicates with alkaline bases alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids*. If a large proportion of hydrochloric acid is added at once to even concentrated solutions of alkaline silicates, the separated silicic acid remains in solution; but if the hydrochloric acid is added gradually drop by drop, whilst stirring the fluid, the greater part of the silicic acid separates as gelatinous hydrate. The more dilute the fluid, the more silicic acid remains in solution, and in *highly* dilute solutions no precipitate is formed. But if the solution of an alkaline silicate, mixed with hydrochloric or nitric acid in excess, is evaporated to dryness, silicic acid separates in proportion as the acid escapes; upon treating the residue with hydrochloric acid and water, the silicic acid remains in the free state (or, if the temperature in the process of drying was restricted to 212°, as hydrate, $H\,O, 4\,Si\,O_2$), as an insoluble white powder. Chloride of ammonium produces in rather concentrated solutions of alkaline silicates precipitates of hydrate of silicic acid.

3. Part of the silicates insoluble in water are decomposed by hydrochloric acid or nitric acid, part of them are not affected by these acids, not even upon boiling. In the decomposition of the former, the greater

portion of the silicic acid separates usually as gelatinous, more rarely as pulverulent hydrate. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated hydrate of silicic acid suspended in it, is evaporated to dryness, the residue heated at a temperature above the boiling point of water until no more acid fumes escape, then moistened with hydrochloric acid, heated with water, and the fluid containing the bases filtered from the residuary insoluble silicic acid.

4. Of the silicates not decomposed by hydrochloric acid, many, *e. g.*, kaolin, are completely decomposed by heating with hydrated sulphuric acid, the decomposition being attended with separation of silicic acid in the pulverulent form; many others are acted upon to some extent by this reagent.

5. If any silicate, reduced to a fine powder, is fused with 4 parts of *carbonate of potassa and soda* until the evolution of carbonic acid has ceased, and the fused mass is then boiled with water, the greater portion of the silicic acid dissolves as alkaline silicate, whilst the alkaline earths, the earths proper, and the heavy metallic oxides are left undissolved. If the fused mass is treated with water, then, without previous filtration, hydrochloric or nitric acid added to strongly acid reaction, and the fluid treated as directed in 3, the silicic acid is left undissolved, whilst the bases are dissolved. If the powdered silicate is fused with 4 parts of hydrate of baryta, the fused mass digested with water, with addition of hydrochloric or nitric acid, and the acid solution treated as directed in 3, the silicic acid separates, and the bases, especially the alkalies, are found in the filtrate.

6. If hydrofluoric acid, in aqueous solution or in the gaseous state, is made to act upon finely pulverized silicates, fluosilicic gas escapes, and the bases are converted into silicofluorides, which upon heating with hydrated sulphuric acid change to sulphates, with evolution of fluosilicic gas. If the powdered silicate is mixed with 5 parts of fluoride of calcium in powder, the mixture made into a paste with hydrated sulphuric acid, and heat applied (best in the open air), until no more fumes escape, the whole of the silicic acid present volatilizes as fluosilicic gas. The bases present are found in the residue as sulphates, mixed with sulphate of lime.

7. If silicic acid or a silicate is fused with *carbonate of soda* on the loop of a platinum wire, a frothing is observed in the fusing bead, owing to the disengagement of carbonic acid. If the proper proportion of carbonate of soda is not exceeded, the bead of silicate of soda formed in the process will remain transparent on cooling.

8. *Phosphate of soda and ammonia*, in a state of fusion, fails nearly altogether to dissolve silicic acid. If therefore silicic acid or a silicate is fused, in small fragments, with phosphate of soda and ammonia on a platinum wire, the bases are dissolved, whilst the silicic acid separates and floats about in the clear bead, as a more or less transparent mass, exhibiting the shape of the fragment used in the experiment.

§ 151.

Recapitulation and remarks.—Free carbonic acid is readily known by its deportment with lime-water; the carbonates are easily detected by the evolution of a nearly inodorous gas, which takes place when they

are treated with acids. When operating upon compounds which, besides carbonic acid, evolve other gases, the disengaged gas is to be tested with lime-water or baryta-water. Silicic acid, both in the free state and in silicates, may usually be readily detected by the reaction with phosphate of soda and ammonia. It differs moreover from all other bodies in the form in which it is always obtained in analyses, by its insolubility in acids (except hydrofluoric acid), and its solubility in boiling solutions of pure alkalies and alkaline carbonates.

SECOND GROUP OF THE INORGANIC ACIDS.

ACIDS WHICH ARE PRECIPITATED BY NITRATE OF SILVER, BUT NOT BY CHLORIDE OF BARIUM: *Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrocyanic Acid, Hydroferro-* and *Hydroferricyanic Acid, Hydrosulphuric Acid.*

§ 152.

The silver compounds corresponding to the acids of this group are insoluble in dilute nitric acid. The acids of this group decompose with metallic oxides, the metals combining with the chlorine, bromine, cyanogen, iodine, or sulphur, whilst the oxygen of the metallic oxide forms water with the hydrogen of the hydracid.

a. HYDROCHLORIC ACID (H Cl).

1. Chlorine is a heavy, yellowish-green gas of a disagreeable, suffocating odor, and which has a most injurious action upon the respiratory organs; it destroys vegetable colors (litmus, indigo-blue, &c.); it is incombustible, and supports the combustion of few bodies only. Minutely-divided antimony, tin, &c., spontaneously ignite in it, being converted into chlorides. It dissolves pretty largely in water; the chlorine water formed has a faint yellowish-green color, smells strongly of the gas, bleaches vegetable colors, is decomposed by the action of light (§ 25), and loses its odor when shaken with mercury; in this process the latter is converted into a mixture of subchloride and metallic mercury. Small quantities of chlorine may be readily detected in a fluid, by adding the latter to a solution of pure protoxide of iron, mixed with sulphocyanide of potassium: the solution is at once colored red by the action of the free chlorine;—or, in the absence of nitric acid, by adding the fluid to a dilute solution of iodide of potassium, mixed with starch-paste. (See § 154, 9.)

2. Hydrochloric acid, at the common temperature and common atmospheric pressure, is a colorless gas, which forms dense fumes in the air, is suffocating and very irritant, and dissolves in water with exceeding facility. The more concentrated solution (fuming hydrochloric acid) loses a large portion of its gas upon heating.

3. The neutral metallic chlorides are readily soluble in water, with the exception of chloride of lead, chloride of silver, and subchloride of mercury; most of the chlorides are white or colorless. Many of them volatilize at a high temperature, without suffering decomposition; others are decomposed upon ignition, and many of them are fixed.

4. *Nitrate of silver* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides white precipitates of CHLORIDE OF SILVER (Ag Cl), which upon exposure to light change first to violet, then to black; they are insoluble in nitric acid, but dissolve readily in

ammonia, as well as in cyanide of potassium, and fuse without decomposition, when heated. (Compare § 114, 7).

5. *Nitrate of suboxide of mercury* and *acetate of lead* produce in solutions containing free hydrochloric acid or metallic chlorides precipitates of SUBCHLORIDE OF MERCURY ($Hg_2 Cl$) and CHLORIDE OF LEAD ($Pb Cl$). For the properties of these precipitates see § 115, 6, and § 116, 7.

6. If hydrochloric acid is heated with *binoxide of manganese*, or a chloride with *binoxide of manganese* and *sulphuric acid*, chlorine gas is evolved, which may be readily recognised by its odor and YELLOWISH-GREEN color.

7. If a metallic chloride is triturated together with *chromate of potassa*, the mixture treated with *concentrated sulphuric acid*, in a tubulated retort, and a gentle heat applied, a deep brownish-red gas is copiously evolved (BICHROMATE OF TERCHLORIDE OF CHROMIUM, $Cr Cl_3$, 2 $Cr O_3$), which condenses into a fluid of the same color, and passes over into the receiver. If this chromate of terchloride of chromium is mixed with ammonia in excess, a yellow-colored liquid is produced; the yellow tint is imparted to the fluid by the chromate of ammonia which forms in this process; upon the addition of an acid, the color of the solution changes to a reddish-yellow, owing to the formation of acid chromate of ammonia.

8. In the metallic chlorides insoluble in water and nitric acid, the chlorine is detected by fusing them with carbonate of soda and potassa, and treating the fused mass with water, which will dissolve, besides the excess of the alkaline carbonate, the chloride of the alkali metal formed in the process of fusion.

9. If in a bead of *phosphate of soda and ammonia* on a platinum wire, *oxide of copper* be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of a substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLORED flame, inclining to PURPLE, will be seen encircling it so long as chlorine is present (*Berzelius*).

§ 153.

b. HYDROBROMIC ACID (H Br).

1. Bromine is a heavy, reddish-brown fluid, of a very disagreeable chlorine-like odor; it boils at 116·6° F., and volatilizes rapidly even at the common temperature. The vapor of bromine is brownish-red. Bromine bleaches vegetable colors like chlorine; it is rather difficultly soluble in water, but dissolves more easily in alcohol, and very readily in ether. The solutions are yellowish-red.

2. Hydrobromic acid gas, its aqueous solution, and the metallic bromides offer in their general deportment a great analogy to the corresponding chlorides.

3. *Nitrate of silver* produces in aqueous solutions of hydrobromic acid or of bromides a yellowish-white precipitate of BROMIDE OF SILVER ($Ag Br$), which changes to violet upon exposure to light; this precipitate is insoluble in nitric acid, and somewhat difficultly soluble in ammonia, but dissolves with facility in cyanide of potassium.

4. *Nitrate of protoxide of palladium*, but not protochloride of palladium, produces in neutral solutions of metallic bromides a reddish-brown

precipitate of PROTOBROMIDE OF PALLADIUM (Pd Br). In concentrated solutions this precipitate is formed immediately, in dilute solutions it makes its appearance only after standing some time.

5. *Nitric acid* decomposes hydrobromic acid and the bromides, with the exception of bromide of silver and bromide of mercury, upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal. The liberated bromine colors the solution yellowish-red. When operating upon bromides in the solid state, brownish-red (if diluted, yellowish-red) vapors of bromine gas escape, emitting the odor of bromine; these vapors, when evolved in sufficient quantity, condense in the cold part of the test-tube to small drops. In the cold, even red fuming nitric acid fails to liberate the bromine contained in rather dilute solutions of metallic bromides.

6. *Chlorine*, in the *gaseous* state or in *solution*, immediately liberates bromine in the solutions of its compounds; the fluid assuming a yellowish-red tint, if the quantity of the bromine present is not too minute. If a solution of this kind is shaken together with some *ether*, it loses its yellow color, the whole of the bromine present dissolving in the ether, which appears now distinctly yellow, even though but a very minute quantity of bromine be present. If the ethereal solution of bromine is mixed with some solution of potassa, and the mixture shaken, the yellow tint disappears again, and the solution now contains bromide of potassium and bromate of potassa. Upon evaporation and subsequent ignition of the residue, the bromate of potassa is converted into bromide of potassium, and the ignited mass may then be further tested as directed in 7. A large excess of chlorine must be avoided in this experiment, as chlorine water of a certain degree of concentration, when shaken with ether, always imparts a faint yellow tint to it.

7. If bromides are heated with *binoxide of manganese* and *concentrated sulphuric acid*, BROWNISH-RED VAPORS OF BROMINE are evolved. If the bromine is present only in very minute quantity, the color of these vapors is not visible. The experiment should, in that case, be conducted in a small retort, and the evolved vapors transmitted through a long glass condenser, and finally received into small test-tubes, containing some starch moistened with water; since

8. If moistened *starch* is brought into contact with free bromine, no matter whether in solution or in the gaseous state, YELLOW BROMIDE OF STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by hermetically sealing the test-tube which contains the moistened starch and the fluid under examination, and then inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine will now, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, after some time, will again disappear.

9. If sulphuric acid is poured over a mixture of a bromide with *chromate of potassa*, and heat is then applied, a brownish-red gas is evolved, exactly as in the case of chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over does not turn yellow, but becomes colorless, upon supersaturation with ammonia.

10. In the metallic bromides which are insoluble in water and nitric acid, the bromine is detected in the same way as the chlorine in the corresponding chlorides.

11. A *phosphate of soda and ammonia bead saturated with oxide of copper*, mixed with a substance containing bromine, and then ignited in the inner blowpipe flame, colors the flame BLUE, inclining to GREEN, more particularly at the edges (*Berzelius*).

§ 154.

c. HYDRIODIC ACID (H I).

1. Iodine is a solid, soft body, of a peculiarly disagreeable odor. It is generally seen in the form of black, shining, crystalline scales. It fuses at a gentle heat; at a somewhat higher temperature, it is converted into iodine vapor, which has a beautiful violet-blue color, and condenses upon cooling to a black sublimate. It is very sparingly soluble in water, but readily in alcohol and ether; the aqueous solution is of a light-brown, the alcoholic and ethereal solutions are a deep red-brown color. Iodine destroys vegetable colors only slowly and imperfectly; it stains the skin brown; with starch it forms a compound of an intensely deep blue color. This compound is formed invariably when iodine vapor or a solution containing free iodine comes in contact with starch, best with starch-paste. It is decomposed by alkalies, and also by chlorine and bromine.

2. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gas; it dissolves copiously in water. The colorless hydrated hydriodic acid turns speedily to a reddish-brown when in contact with the air, owing to the formation of water, and a solution of iodine in hydriodic acid.

3. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides have characteristic colors.

4. Nitrate of silver produces in aqueous solutions of hydriodic acid and of iodides yellowish-white precipitates of IODIDE OF SILVER (Ag I), which blacken on exposure to light; these precipitates are insoluble in dilute nitric acid, and *very sparingly soluble in ammonia*, but dissolve readily in cyanide of potassium.

5. *Protochloride of palladium* and *nitrate of protoxide of palladium* produce even in very dilute solutions of hydriodic acid or metallic iodides a brownish-black precipitate of PROTIODIDE OF PALLADIUM, which dissolves to a trifling extent in saline solutions (solution of chloride of sodium, chloride of magnesium, &c.), but is insoluble or nearly so in dilute cold hydrochloric and nitric acids.

6. A solution of 1 part of *sulphate of oxide of copper* and 2½ parts of *sulphate of protoxide of iron* throws down from neutral aqueous solutions of the iodides SUBIODIDE OF COPPER (Cu_2 I), in the form of a dirty-white precipitate. The addition of ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent.

7. Pure *nitric acid*, free from nitrous acid, decomposes hydriodic acid or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But *nitrous acid* and *hyponitric acid* decompose hydriodic acid and iodides with the greatest facility even in the most dilute solutions. Colorless solutions of iodides

therefore acquire immediately a brownish-red color, upon addition of some red-fuming nitric acid, or a mixture of this with concentrated sulphuric acid or, better still, a solution of hyponitric acid in hydrated sulphuric acid or nitrite of potassa and some sulphuric or hydrochloric acid. From more concentrated solutions the iodine separates under these circumstances in the form of small black plates or scales, whilst nitric oxide gas and iodine vapors escape.

8. As the blue coloration of iodide of starch remains still visible in much more highly dilute solutions than the yellow color of solutions of iodine in water, the delicacy of the reaction just now described (7) is considerably heightened by mixing the fluid to be tested for iodine first with some thin, clear *starch-paste*, then adding one or two drops of dilute sulphuric acid, to make the fluid acid, and adding finally one or the other of the reagents given in 7. Of the solution of hyponitric acid in sulphuric acid a single drop on a glass rod suffices to produce the reaction most distinctly. I can therefore strongly recommend this reagent, which was first proposed by *Otto*. Red fuming nitric acid must be added in somewhat larger quantity, to call forth the reaction in its highest intensity; this reagent therefore is not well adapted to detect *very minute* quantities of iodine. The reaction with nitrite of potassa also is very delicate. The fluid to be tested is mixed with dilute sulphuric acid or with hydrochloric acid to distinctly acid reaction, and a drop or two of a concentrated solution of nitrite of potassa is then added. In cases where the quantity of iodine present is very minute, the fluid turns reddish, instead of blue. An excess of the fluid containing nitrous acid or hyponitric acid does not materially impair the delicacy of the reaction. As iodide of starch dissolves in hot water to a colorless liquid, the fluids must of necessity be cold; the colder they are, the more delicate the reaction.

9. *Chlorine gas* and *chlorine water* decompose compounds of iodine also, setting the iodine free; but if the chlorine is applied in excess, the liberated iodine combines with it to colorless chloride of iodine. A dilute solution of a metallic iodide, mixed with starch-paste, acquires therefore upon addition of a little chlorine water at once a blue tint, but becomes colorless again upon addition of more chlorine water. As it is therefore difficult not to exceed the proper limit, especially where the quantity of iodine present is only small, chlorine water is not well adapted for the detection of minute quantities of iodine.

10. If a solution in which iodine has been set free by nitrous acid, chlorine, &c., is mixed with *ether*, and the mixture shaken, the ether dissolves the liberated iodine, and acquires thereby a reddish-brown or yellow color. The color imparted to the ether by iodine is much more intense than that imparted to that fluid by an equal quantity of bromine. If the solution is mixed with some *chloroform* or *bisulphide of carbon*, and the mixture shaken, leaving a few drops of the reagent undissolved, these will subside to the bottom of the fluid, exhibiting a lighter or darker red color. This reaction also is very delicate.

11. If metallic iodides are heated with *concentrated sulphuric acid*, or with *sulphuric acid* and *binoxide of manganese*, or with *sulphuric acid* and *chromate of potassa*, iodine separates, which may be known by the color of its vapor and, in the case of very minute quantities, also by its action upon a slip of paper coated with starch-paste.

12. The iodides which are insoluble in water and nitric acid comport

themselves upon fusion with *carbonate of soda and potassa* in the same manner as the corresponding chlorides.

13. A *phosphate of soda and ammonia bead*, saturated with oxide of copper, when mixed with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense GREEN color to the flame.

§ 155.

d. HYDROCYANIC ACID (H Cy).

1. Cyanogen is a colorless gas of a peculiar, penetrating odor; it burns with a crimson flame, and is pretty soluble in water.

2. Hydrocyanic acid is a colorless, volatile, inflammable liquid, the odor of which resembles that of bitter almonds; it is miscible with water in all proportions; in the pure state it speedily suffers decomposition. It is extremely poisonous.

3. The cyanides with alkalies and alkaline earths are soluble in water; the solutions smell of hydrocyanic acid. They are readily decomposed by acids, even by carbonic acid; but ignition fails to decompose them, if the access of air is precluded. When fused with oxides of lead, copper, antimony, tin, &c., the cyanides reduce these oxides, and are converted into cyanates. Only a few of the cyanides with heavy metals are soluble in water; all of them are decomposed upon ignition, the cyanides of the noble metals being converted into cyanogen gas and metal, the cyanides of the other heavy metals into nitrogen gas and metallic carbides. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. But hydrochloric acid and hydrosulphuric acid decompose most of them readily and completely.

4. The cyanides have a great tendency to combine with each other; hence most of the cyanides of the heavy metals dissolve in cyanide of potassium. The resulting compounds are either:

a. True double salts, compounds of the second class, *e.g.*, K Cy + Ni Cy. From solutions of such double salts, acids, by decomposing the cyanide of potassium, precipitate the metallic cyanide which was combined with it.—Or they are:

b. Simple haloid salts, compounds of the first class, in which a metal, *e. g.*, potassium, is combined with a compound radical consisting of cyanogen and another metal (iron, cobalt, manganese, chromium). Compounds of this kind are the ferro- and ferricyanide of potassium, $K_2\,Cy_3\,Fe$ or K_2 Cfy, and $K_3\,Cy_6\,Fe_2$ or K_3 Cfdy, cobalticyanide of potassium, $K_3\,Cy_6\,Co_2$, &c. From solutions of compounds of this nature dilute acids do not separate metallic cyanides in the cold. If the potassium is replaced by hydrogen, peculiar hydracids are formed, which must not be confounded with hydrocyanic acid.

We will now first consider the reaction of hydrocyanic acid and the simple cyanides, then, in an appendix to this paragraph, those of hydroferro- and hydroferricyanic acid.

5. *Nitrate of silver* produces in solutions of free hydrocyanic acid and of cyanides of the alkali metals white precipitates of CYANIDE OF SILVER (Ag Cy), which are readily soluble in cyanide of potassium, dissolve with some difficulty in ammonia, and are insoluble in nitric acid; these pre-

cipitates are decomposed upon ignition, leaving metallic silver with some paracyanide of silver.

6. If solution of *sulphate of protoxide of iron* which has been for some time in contact with the air is added to a solution of free hydrocyanic acid, no alteration takes place; but if *solution of potassa* or *soda* is now added, a bluish-green precipitate forms, which consists of a mixture of Prussian-blue ($Fe_4\ Cfy_3$), and hydrate of protosesquioxide of iron. Upon now adding hydrochloric acid (best after previous application of heat), the hydrate of protosesquioxide of iron dissolves, whilst the PRUSSIAN-BLUE remains undissolved. If only a very minute quantity of hydrocyanic acid is present, the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it. The same reactions are observed when sulphate of protoxide of iron is added to the solution of an alkaline cyanide.

7. If a liquid containing a small quantity of hydrocyanic acid or cyanide of potassium is mixed with a small quantity (one or two drops) of yellow sulphide of ammonium and a trace of ammonia, and the mixture warmed in a porcelain dish until it has become colorless, sulphocyanide of ammonium is formed, and the fluid, after being acidified with hydrochloric acid, acquires a blood-red tint upon addition of sesquichloride of iron (*Liebig*). This reaction is exceedingly delicate. The following formula expresses the transformation of hydrocyanic acid into sulphocyanide of ammonium: $N\,H_4, S_5 + 2\,(N\,H_4, O) + 2\,H\,Cy = 2\,(N\,H_4, Cy\,S_2) + N\,H_4, S + 2\,H\,O$. If an acetate is present, the reaction takes place only upon addition of more hydrochloric acid.

8. Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. To detect cyanogen in that compound, the solution is mixed with hydrosulphuric acid: sulphide of mercury precipitates, and the solution contains free hydrocyanic acid. In solid cyanide of mercury the cyanogen is most readily detected by heating in a glass tube. Compare 3.

Appendix.

a. Hydroferrocyanic acid ($2\,H\,Cfy$). Hydroferrocyanic acid is soluble in water. In solutions of this acid or of soluble ferrocyanides, *sesquichloride of iron* produces a blue precipitate of FERROCYANIDE OF IRON ($Fe_4\ Cfy_3$); *sulphate of oxide of copper*, a brownish-red precipitate of FERROCYANIDE OF COPPER ($Cu_2\ Cfy$); *nitrate of silver*, a white precipitate of FERROCYANIDE OF SILVER ($Ag_2\ Cfy$), which is insoluble in nitric acid and in ammonia, but dissolves in cyanide of potassium. Insoluble ferrocyanides of metals are decomposed by boiling with solution of soda, ferrocyanide of sodium being formed and the oxides thrown down. When heated with 3 parts of sulphate and 1 part of nitrate of ammonia, they yield sulphates of the metals contained in them, the whole of the cyanogen volatilizing in form of cyanide of ammonium and the products of its decomposition (*Bolley*).

b. Hydroferricyanic acid. In the aqueous solutions of hydroferricyanic acid and its salts, *sesquichloride of iron* produces no blue precipitate; but *sulphate of protoxide of iron* produces a blue precipitate of PROTO-FERRICYANIDE OF IRON ($3\,Fe, Cfdy$); *sulphate of copper*, a yellowish-green precipitate of FERRICYANIDE OF COPPER ($3\,Cu, Cfdy$), which is insoluble

in hydrochloric acid; *nitrate of silver*, an orange-colored precipitate of FERRICYANIDE OF SILVER (3 Ag, Cfdy), which is insoluble in nitric acid, but dissolves readily in ammonia and in cyanide of potassium. The insoluble ferricyanides of metals are decomposed by boiling with solution of soda, the metallic oxides being thrown down; in the fluid filtered off from them, either ferrocyanide of sodium alone is found, or a mixture of ferro- with ferricyanide of sodium. By heating with sulphate and nitrate of ammonia the ferricyanides are decomposed the same as the ferrocyanides.

§ 156.

e. HYDROSULPHURIC ACID (H S).

Sulphuretted Hydrogen.

1. Sulphur is a solid, brittle, friable, tasteless body, insoluble in water. It occurs occasionally in the form of yellow or brownish crystals, or crystalline masses of a yellow or brownish color, and occasionally in that of a yellow or yellowish-white or grayish-white powder. It melts at a moderate heat; upon the application of a stronger heat it is converted into brownish-yellow vapors, which, in cold air, condense to a yellow powder, and on the sides of the vessel, to drops. Heated in the air, it burns with bluish flame to sulphurous acid, which betrays its presence in the air at once by its suffocating odor. Concentrated nitric acid, nitrohydrochloric acid, and a mixture of chlorate of potassa and hydrochloric acid dissolve sulphur gradually, with the aid of a moderate heat, and convert it into sulphuric acid; in boiling solution of soda sulphur dissolves to a yellow fluid, which contains sulphide of sodium and hyposulphite of soda; in ammonia sulphur is insoluble.

2. Hydrosulphuric acid, at the common temperature and under common atmospheric pressure, is a colorless, inflammable gas, soluble in water, and which may be readily recognised by its characteristic smell of rotten eggs; it transiently imparts a red tint to litmus paper.

3. Of the sulphides only those with alkalies and alkaline earths are soluble in water. These, and the sulphides of iron, manganese, and zinc, are decomposed by dilute mineral acids, with evolution of hydrosulphuric acid gas, which may be readily detected by its peculiar smell, and by its action upon solution of lead (see 4). The decomposition of higher sulphides is attended also with separation of sulphur in a finely-divided state; the white precipitate may be readily distinguished from similar precipitates by its deportment on heating. Part of the sulphides of the metals of the fifth and sixth groups are decomposed by concentrated and boiling hydrochloric acid, with evolution of hydrosulphuric acid gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury resist the action of both acids, but dissolve readily in nitrohydrochloric acid. Upon the solution of sulphides in nitric acid, and in nitrohydrochloric acid, sulphuric acid is formed, and the process of solution is moreover attended, in most cases, with separation of sulphur, which is readily recognised by its color and by its deportment upon heating. Many metallic sulphides, more especially of a higher degree of sulphuration, give a sublimate of sulphur when heated in a test-tube.

4. If hydrosulphuric acid, in the gaseous state or in solution, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates of

SULPHIDE OF SILVER or SULPHIDE OF LEAD are formed (see § 114 and § 116). In cases therefore where the odor of the gas fails to afford sufficient proof of the presence of hydrosulphuric acid, these reagents will remove all doubt. If the hydrosulphuric acid is present in the gaseous form, the air suspected to contain it is tested by placing in it a small slip of paper moistened with solution of neutral acetate of lead and a little ammonia; if the gas is present, the slip becomes covered with a thin, brownish-black, shining film of sulphide of lead. To detect a trace of an alkaline sulphide in presence of a free alkali or an alkaline carbonate, the best way is to mix the fluid with a solution of oxide of lead in solution of soda, which is prepared by mixing solution of acetate of lead with solution of soda until the precipitate which forms at first is redissolved.

5. If a fluid containing hydrosulphuric acid or an alkaline sulphide is mixed with solution of soda, then with *nitroprusside of sodium,** it acquires a fine reddish-violet tint. The reaction is very delicate; but that with solution of oxide of lead in solution of soda is still more sensitive.

6. If metallic sulphides are exposed to the *oxidizing flame of the blowpipe*, the sulphur burns with a blue flame, emitting at the same time the well-known odor of sulphurous acid. If a metallic sulphide is heated in a glass tube open at both ends, in the upper part of which a slip of blue litmus paper is inserted, and the tube is held in a slanting position during the operation, the escaping sulphurous acid reddens the litmus paper.

7. If a finely-pulverized metallic sulphide is boiled in a porcelain dish with solution of potassa, and the mixture heated to incipient fusion of the hydrate of potassa, or if the test specimen is fused in a platinum spoon with hydrate of potassa, and the mass is, in either case, dissolved in a little water, a piece of bright silver (a polished coin) put into the solution, and the fluid warmed, a brownish-black film of sulphide of silver forms on the metal. This film may be removed afterwards by rubbing the metal with leather and quicklime (*v. Kobell*).

§ 157.

Recapitulation and remarks.—Most of the acids of the first group are also precipitated by nitrate of silver, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are *soluble* in dilute nitric acid, whilst the latter are *insoluble* in that menstruum. The presence of hydrosulphuric acid interferes more or less with the testing for the other acids of the second group; this acid must therefore, if present, be removed first before the testing for the other acids can be proceeded with. The removal of the hydrosulphuric acid, when present in the free state, may be effected by simple ebullition; and when present in the form of an alkaline sulphide, by the addition of a metallic salt, such as will not precipitate any of the other acids, or at least will not precipitate them from acid solutions. Hydriodic and hydrocyanic acids may be detected, even in presence of hydrochloric or hydrobromic acid, by the equally characteristic and delicate reactions with starch (with addition of a fluid containing nitrous acid), and with solution of protosesquioxide of iron. But the detection

* Nitroprusside of sodium being a reagent which can very well be dispensed with, I have omitted giving it a place among the reagents.

of chlorine and bromine is more or less difficult in presence of iodine and cyanogen. These latter must therefore, if present, be removed first before the proper tests for chlorine and bromine can be applied. The separation of the cyanogen may be readily effected by converting the whole of the radicals present into salts of silver, and igniting the mixed compound produced: the cyanide of silver is decomposed in this process, whilst the chloride, bromide, and iodide of silver remain unaltered. Upon fusing the ignited residue with carbonate of soda and potassa, and boiling the fused mass with water, chloride, bromide, and iodide of the alkali metals are obtained in solution.

Bromine in presence of iodine and chlorine may, according to experiments recently made by me, be identified by the following simple operation: Mix the fluid with a few drops of dilute sulphuric acid, then with some starch-paste, and add a little red fuming nitric acid or, better still, a solution of hyponitric acid in sulphuric acid, whereupon the iodine reaction will show itself immediately. Add now chlorine water drop by drop until that reaction has disappeared; and then add some more chlorine water to set the bromine also free, which may then be separated and identified by means of ether. Or the liberated iodine may also be removed first by means of ether, chloroform, or bisulphide of carbon, and the fluid then tested for bromine, by means of chlorine water and ether. The iodine may be separated from the chlorine and bromine, by treating the mixed silver compound with ammonia, but more accurately by precipitating the iodine as protiodide of copper. From bromine the iodine is separated most accurately by protochloride of palladium, which only precipitates the iodine; from chlorine it is separated by nitrate of protoxide of palladium. Metallic chlorides are detected in presence of metallic bromides by the reaction with chromate of potassa and sulphuric acid.

§ 158.

Supplement to the Second Group of the Inorganic Acids.

1. *Nitrous acid* ($N O_3$). Nitrous acid, in the free state, at the common temperature, is a brownish-red gas. In contact with water it is converted into nitric acid, which dissolves, and nitric oxide gas, which remains undissolved ($3 N O_3 = N O_5 + 2 N O_2$). The nitrites are decomposed by ignition; many of them are soluble in water. When nitrites or concentrated solutions of nitrites are treated with dilute sulphuric acid, it is not nitrous acid gas which is evolved, but nitric oxide gas, attended with formation of nitric acid. In solutions of nitrites of the alkalies *nitrate of silver* produces a white precipitate, which dissolves in a very large proportion of water, especially upon application of heat; *sulphate of protoxide of iron*, upon addition of a small quantity of acid, produces a dark blackish-brown coloration, which is due to nitric oxide gas in the solution of the sulphate of protoxide of iron. *Hydrosulphuric acid* produces in neutral as well as in acid solutions copious precipitates of sulphur, attended with formation of nitrate of ammonia. Solution of *iodide of potassium*, mixed with starch-paste, is immediately colored blue by nitrites, upon addition of hydrochloric acid. For the deportment of nitrites with solutions of cobalt, see § 108, 10.

2. *Hypochlorous acid* (Cl O). Hypochlorous acid, at the common

temperature, is a deep yellowish-green gas of a disagreeable, irritating odor, similar to that of chlorine. It dissolves in water; the dilute solution bears distillation. The hypochlorites are usually found in combination with metallic chlorides, as is the case, for instance, in chloride of lime, *eau de Javelle*, &c. The solutions of hypochlorites undergo alteration by boiling, the hypochlorite being resolved into chloride of the metal and chlorate of the oxide, attended, in the case of concentrated, but not in that of dilute solutions, with evolution of oxygen. If a solution of chloride of lime, &c., is mixed with hydrochloric acid or sulphuric acid, chlorine is disengaged, whilst addition of a little nitric acid leads to the liberation of hypochlorous acid. *Nitrate of silver* throws down from solution of chloride of lime chloride of silver; *nitrate of lead* produces a precipitate which from its original white changes gradually to orange-red, and ultimately, owing to formation of binoxide, to brown; *salts of protoxide of manganese* give brown-black precipitates of hydrate of binoxide of manganese, &c. Solutions of *litmus* and *indigo* are decolorized even by the alkaline solutions of hypochlorites, but still more rapidly and completely upon addition of an acid.

THIRD GROUP OF THE INORGANIC ACIDS.

ACIDS WHICH ARE NOT PRECIPITATED BY SALTS OF BARYTA NOR BY SALTS OF SILVER: *Nitric Acid, Chloric Acid.*

§ 159.

a. NITRIC ACID ($N\,O_5$).

1. Anhydrous nitric acid crystallizes in six-sided prisms. It fuses at 85·2° F., and boils at about 113° F. (*Deville*). The pure hydrate is a colorless, exceedingly corrosive fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors nitrogenous matter intensely yellow. Hydrate of nitric acid containing nitrous acid has a red color.

2. All the neutral salts of nitric acid are soluble in water; only some of the basic nitrates are insoluble in this menstruum. All nitrates without exception undergo decomposition at an intense red heat. Those with alkaline bases yield at first oxygen, and change to nitrites, which are then further resolved into oxygen and nitrogen; the others yield oxygen and nitrous or hyponitric acid.

3. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion, DEFLAGRATION takes place, *i. e.*, the charcoal burns at the expense of the oxygen of the nitric acid, the combustion being attended with vivid scintillation.

4. If a mixture of a nitrate with *cyanide of potassium* in powder is heated on a platinum plate, a vivid DEFLAGRATION will ensue, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

5. If the solution of a nitrate is mixed with an equal volume of concentrated sulphuric acid, free from nitric and hyponitric acid, the mixture allowed to cool, and a concentrated solution of *sulphate of protoxide of iron* then cautiously added to it so that the fluids do not mix, the stratum, where the two fluids are in immediate contact, shows a brown or, in cases

where only a very minute quantity of nitric acid is present, a reddish color. In this process the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combining with the protoxide and converting a portion of it into sesquioxide, whilst the remaining nitric oxide combines with the remaining portion of the protoxide of iron, and forms with it a peculiar compound, which dissolves in water, imparting a brownish-black color to the fluid.

6. If to the solution of a nitrate some sulphuric acid is added, and as much *solution of indigo* in sulphuric acid as will impart a faint light-blue tint to the fluid, and the mixture is heated to boiling, the blue color changes to a faint yellowish tint, or the fluid becomes colorless. This change of color is owing to the oxidation of the indigo at the expense of the oxygen of the nitric acid which is liberated by the sulphuric acid. It must be borne in mind, however, that several other substances also cause decoloration of solution of indigo—free chlorine more particularly produces this effect.

7. If a nitrate is mixed with *copper filings*, and the mixture heated in a test-tube with concentrated sulphuric acid, the air in the tube acquires a yellowish-red tint, owing to the nitric oxide gas which is liberated upon the oxidation of the copper by the nitric acid, combining with the oxygen of the air to nitrous acid. The coloration may be observed most distinctly by looking lengthways through the tube.

8. If a little *brucia* is dissolved in concentrated sulphuric acid, and a little of a fluid containing nitric acid added to the solution, the latter immediately acquires a magnificent red color. This reaction is exceedingly characteristic.

9. Very minute quantities of nitric acid may be detected also, by fusing the substance under examination with carbonate of soda and potassa at a moderate heat, extracting the mass, after cooling, with water, filtering, adding the filtrate to a solution of iodide of potassium mixed with starch-paste, and then adding hydrochloric acid. In making the experiment, the operator has to ascertain whether the solution of iodide of potassium mixes with the hydrochloric acid without being colored blue by it, since this blue coloration would indicate the presence of iodic acid in the iodide of potassium, or of free chlorine in the hydrochloric acid.

§ 160.

b. Chloric Acid ($Cl\ O_5$).

1. Chloric acid, in its most highly concentrated solution, is a yellow, oily fluid; its odor resembles that of nitric acid. It first reddens litmus and then bleaches it. Dilute chloric acid is colorless and inodorous.

2. All chlorates are soluble in water. When chlorates are heated to redness, the whole of their oxygen escapes and metallic chlorides remain.

3. Heated with *charcoal* or some organic substance, the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. If a mixture of a chlorate with *cyanide of potassium* is heated on platinum foil, DEFLAGRATION takes place, attended with strong detonation and ignition, even though the chlorate be present only in very small quantity. This experiment should be made with very minute quantities only.

5. Free chloric acid oxidizes and decolorizes *indigo* in the same manner as nitric acid; consequently if the solution of a chlorate is mixed with sulphuric acid and solution of indigo, and the mixture heated, the same reaction is observed as with nitric acid (see § 159, 6).

6. If the solution of a chlorate is colored light-blue with *solution of indigo* in sulphuric acid, a little dilute sulphuric acid added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the color of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, thus setting free chlorine or a lower oxide of it, which then decolorizes the indigo.

7. When chlorates are treated with *hydrochloric acid*, the constituents of the two acids transpose, forming water, chlorine, and chlorochloric acid ($2\,Cl\,O_5,\ Cl\,O_3$). Application of heat promotes the reaction. The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas of a very disagreeable odor resembling that of chlorine; the hydrochloric acid acquires a greenish-yellow color.

8. *Concentrated sulphuric acid*, poured over a chlorate, converts two-thirds of the metallic oxide into a sulphate and the remaining one-third into perchlorate; this conversion is attended, moreover, with liberation of chlorochloric acid, which imparts an intensely yellow tint to the sulphuric acid, and betrays its presence also by its odor and the greenish color of the evolved gas. [$3\,(K\,O,\ Cl\,O_5) + 4\,S\,O_3 = (K\,O,\ 2\,S\,O_3) + K\,O,\ Cl\,O_7 + (Cl\,O_5,\ Cl\,O_3)$]. The application of heat must be avoided in this experiment, and the quantities operated upon should be very small, since otherwise the decomposition might take place with such violence as to cause an explosion.

§ 161.

Recapitulation and remarks.—Of the reactions which have been suggested to effect the detection of nitric acid, those with sulphate of protoxide of iron and sulphuric acid, with copper filings and sulphuric acid, with brucia, and also those based upon the reduction of the nitrates to nitrites, give the most positive results; with regard to deflagration with charcoal, detonation with cyanide of potassium, and decoloration of solution of indigo, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only when no chloric acid is present. The presence of free nitric acid in a fluid may be detected by evaporating the fluid, in a porcelain dish on the water-bath, to dryness, having first thrown in a few quill-cuttings: yellow coloration of these indicates the presence of nitric acid (*Runge*). The best way to ascertain whether chloric acid is present or not, is to ignite the sample under examination, dissolve the mass, and test the solution with nitrate of silver. If a chlorate is present, this is converted into a chloride upon ignition, and nitrate of silver will now precipitate chloride of silver from the solution. However, the process is thus simple only if no chloride is present along with the chlorate. But in presence of a chloride, the latter must be removed first by adding nitrate of silver to the solution as long as a precipitate continues to form, and filtering the fluid from the precipitate; the filtrate is then, after addition of pure carbonate of soda, evaporated to dryness, and the residue ignited. It is, however, generally unnecessary to pursue this circuitous

way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid.

II. Organic Acids.

First Group.

Acids which are invariably precipitated by Chloride of Calcium: *Oxalic Acid, Tartaric Acid* (*Paratartaric or Racemic Acid*), *Citric Acid, Malic Acid.*

§ 162.

a. Oxalic Acid.

For the reactions of oxalic acid I refer to § 146.

b. Tartaric Acid ($2HO, C_8H_4O_{10}$).

1. The hydrate of tartaric acid forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in spirit of wine. Tartaric acid when heated fuses at first, and afterwards becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar.

2. The tartrates with alkaline base are soluble in water, and so are those with the metallic oxides of the third and fourth groups; those of the tartrates which are insoluble in water dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness; charcoal separates, and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of a tartrate, solution of *sesquioxide of iron, protoxide of manganese* or *alumina* is added, and then ammonia or potassa, no precipitation of sesquioxide of iron, protoxide of manganese or alumina will ensue, since the double tartrates formed are not decomposed by alkalies. Tartaric acid prevents also the precipitation of several other oxides by alkalies.

4. Free tartaric acid produces with *salts of potassa*, and more particularly with the acetate, a difficultly soluble precipitate of bitartrate of potassa. A similar precipitate is formed when acetate of potassa and free acetic acid are added to the solution of a neutral tartrate. The acid tartrate of potassa dissolves readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The separation of the bitartrate of potassa precipitate is greatly promoted by shaking, or by rubbing the sides of the vessel with a glass rod.

5. *Chloride of calcium* throws down from solutions of neutral tartrates a white precipitate of tartrate of lime ($2CaO, C_8H_4O_{10} + 8$ aq.). Presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid or friction on the sides of the vessel promotes the separation of the precipitate. The precipitate is crystalline or it invariably assumes a crystalline form after some time; it dissolves in a cold not over dilute solution of potassa or soda, pretty free from carbonic acid, to a clear fluid. But upon boiling this solution, the dissolved tartrate of lime separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* produces in solutions of neutral tartrates—and also in a solution of free tartaric acid, if added to alkaline reaction—white precipitates which, flocculent at first, assume afterwards a crystalline form; so long as they remain flocculent, they are readily dissolved by tartaric acid as well as by solution of chloride of ammonium. From these solutions the tartrate of lime separates again, after the lapse of several hours, in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of sulphate of lime* fails to produce a precipitate in a solution of tartaric acid; in solutions of neutral tartrates it produces a trifling precipitate after the lapse of some time.

8. If solution of ammonia is poured upon even a very minute quantity of tartrate of lime, a small fragment of crystallized *nitrate of silver* added, and the mixture slowly and gradually heated, the sides of the test-tube are covered with a bright coating of metallic silver. If instead of a crystal, solution of nitrate of silver be used, or heat be applied more rapidly, the reduced silver will separate in pulverulent form (*Arthur Casselmann*).

9. *Acetate of lead* produces white precipitates in solutions of tartaric acid and its salts. The precipitate ($2\,PbO, C_8H_4O_{10}$) dissolves readily in nitric acid and in ammonia.

10. *Nitrate of silver* does not precipitate free tartaric acid; but in solutions of neutral tartrates it produces a white precipitate of TARTRATE OF SILVER ($2\,AgO, C_8H_4O_{10}$), which dissolves readily in nitric acid and in ammonia; upon boiling it turns black, owing to ensuing reduction of the silver to the metallic state.

11. Upon heating hydrated tartaric acid, or a tartrate, with hydrate of sulphuric acid, the sulphuric acid acquires a brown color almost simultaneously with the evolution of gas.

§ 163.

c. Citric Acid ($3\,HO, C_{12}H_5O_{11}$).

1. Crystallized citric acid, obtained by the cooling of its solution, has the formula, $3\,HO, C_{12}H_5O_{11} + 2\,aq.$ It crystallizes in pellucid, colorless, and inodorous crystals of an agreeable acid taste, which dissolve readily in water and in spirit of wine. Heated to 212° F., the crystallized acid loses its water of crystallization; when subjected to the action of a stronger heat, it fuses at first, and afterwards carbonizes, with evolution of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization.

2. The citrates with alkaline base are readily soluble in water, as well in the neutral as in the acid state; the same applies to the compounds of citric acid with such of the metallic oxides as are weak bases, sesquioxide of iron, for instance. Citrates, like tartrates, and for the same reason, prevent the precipitation of sesquioxide of iron, protoxide of manganese, alumina, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solution of free citric acid, even upon boiling; but a precipitate of NEUTRAL CITRATE OF LIME ($3\,CaO, C_{12}H_5O_{11} + 4\,aq.$) forms immediately upon saturating with potassa or soda the concentrated solution of citric acid, mixed with chloride of calcium in excess. The precipitate is insoluble in potassa, but it dissolves readily in solution of chloride of ammonium; upon boil-

ing this chloride of ammonium solution, neutral citrate of lime of the same composition separates again in the form of a white crystalline precipitate, which, however, is now no longer soluble in chloride of ammonium. If a solution of citric acid mixed with chloride of calcium is saturated with ammonia, a precipitate will form in the cold only after many hours' standing; but upon boiling the clear fluid, neutral citrate of lime of the properties just stated will suddenly precipitate. When citrate of lime is heated with ammonia and nitrate of silver, no reduction of the latter salt ensues.

4. *Lime-water* produces no precipitate in cold solutions of citric acid or of citrates. But upon heating the solution to boiling, with a tolerable excess of hot prepared lime-water, a white precipitate of CITRATE OF LIME is formed, of which the greater portion redissolves upon cooling.

5. *Acetate of lead*, when added in excess to a solution of citric acid, produces a white precipitate of CITRATE OF LEAD ($3\,PbO, C_{12}H_5O_{11}$), which, after washing, dissolves readily in ammonia.

6. *Nitrate of silver* produces in solutions of neutral citrates of the alkalies a white, flocculent precipitate of CITRATE OF SILVER ($3\,AgO, C_{12}H_5O_{11}$), which does not become black on boiling.

7. Upon heating citric acid or citrates with concentrated sulphuric acid, carbonic oxide and carbonic acid escape at first, the sulphuric acid retaining its natural color; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

§ 164.

d. MALIC ACID ($2\,HO, C_8H_4O_8$),

1. Hydrate of malic acid crystallizes with great difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Exposed to a temperature of 356° F., malic acid is resolved into MALÆIC ACID ($2\,HO, C_8H_2O_6$) and FUMARIC ACID ($2\,HO, C_8H_2O_6$), which latter is upon continued application of heat also converted into the former. This deportment of malic acid is highly characteristic. If the experiment is made in a small spoon, pungent acid vapors of malæic acid are evolved with frothing effervescence. If the experiment is made in a small tube, these fumes condense to crystals in the colder part of the tube.

2. Malic acid forms with most bases salts soluble in water. The acid malate of potassa is not very difficultly soluble in water. Malic acid prevents, like tartaric acid, the precipitation of sesquioxide of iron, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solutions of free malic acid. Even after saturation with potassa or soda no precipitate is formed. But upon boiling, a precipitate of MALATE OF LIME ($2\,CaO, C_8H_4O_8 + 6$ aq.) separates from concentrated solutions. If the precipitate is dissolved in a very little hydrochloric acid, ammonia added to the solution, and the fluid boiled, the malate of lime separates again; but if it is dissolved in a somewhat larger quantity of hydrochloric acid, it will not reprecipitate, after addition of ammonia in excess, even upon continued boiling. Alcohol precipitates it immediately from a solution of the kind. Malate of lime, when heated with ammonia and nitrate of silver, fails to affect the reduction of the latter to the metallic state.

4. *Lime-water* produces no precipitate, either in solutions of free malic acid or in solutions of malates.

5. *Acetate of lead* throws down from solutions of malic acid and of malates a white precipitate of MALATE OF LEAD ($2.PbO, C_8H_4O_8 + 6$ aq.). The precipitation is the most complete, if the fluid is neutralized by ammonia, as the precipitate is slightly soluble in free malic acid and acetic acid, and also in ammonia. If the fluid in which the precipitate is suspended is heated to boiling, a portion of the precipitate dissolves, the remainder fuses to a mass resembling resin melted under water. This reaction is distinctly marked only when the malate of lead is tolerably pure; if mixed with other salts of lead—if, for instance, ammonia is added to alkaline reaction, it is only imperfect or fails altogether to make its appearance.

6. *Nitrate of silver* throws down from solutions of neutral malates of the alkalies a white precipitate of MALATE OF SILVER, which upon boiling turns a little gray.

7. Upon heating malic acid with concentrated sulphuric acid, carbonic acid and carbonic oxide gas are evolved at first; the fluid then turns brown and ultimately black, with evolution of sulphurous acid.

§ 165.

Recapitulation and remarks.—Of the organic acids of this group, *oxalic acid* is characterized by the precipitation of its lime-salt from its solution in hydrochloric acid by ammonia, and also by acetate of soda, as well as by the immediate precipitation of the free acid by solution of sulphate of lime. *Tartaric acid* is characterized by the difficult solubility of the acid potassa salt, the solubility of the lime salt in cold solution of soda and of potassa, the deportment of the lime salt with ammonia and nitrate of silver, and the peculiar odor which the acid and its salts emit upon heating. *Citric acid* is most strongly characterized by its deportment with lime-water, or with chloride of calcium and ammonia in presence of chloride of ammonium. *Malic acid* would be sufficiently characterized by the deportment of malate of lead when heated under water, were this reaction more sensitive, and not so easily prevented by the presence of other acids. The safest means of identifying malic acid is to convert it into malæic acid by heating in a glass tube; but this conversion can be effected successfully only with pure hydrate of malic acid. Malate of lead is difficultly soluble in ammonia, whilst citrate of lead dissolves readily in that agent; this different deportment of the lead salts of the two acids affords also a means of distinguishing between them. If only one of the four acids is present in a solution, lime-water will suffice to indicate which of the four is present; since malic acid is not precipitated by this reagent, citric acid only upon boiling, tartaric acid and oxalic acid already in the cold; and the tartrate of lime redissolves upon addition of chloride of ammonium, whilst the oxalate does not. If the four acids together are present in a solution, the oxalic acid and tartaric acid are precipitated first by chloride of calcium and ammonia, in presence of chloride of ammonium (the tartrate of lime separates under these circumstances completely only after some time; it is separated from the oxalate by treating with solution of soda); the citrate of lime is then thrown down by boiling, and the malate finally by means of spirit of wine. The precipitate produced by spirit of wine

must never be taken positively for malate of lime, without further proof, since the sulphate and other salts of lime are also precipitated by that agent under the same circumstances. Positive conviction can only be attained by the production of hydrate of malic acid from the lime-salt. To effect this, the precipitate is dissolved in acetic acid, spirit of wine added, and the fluid filtered, if necessary. The filtrate is precipitated with acetate of lead, the fluid neutralized with ammonia, the precipitate washed, stirred in water, decomposed by hydrosulphuric acid, and the filtrate evaporated to dryness.

§ 166.

Appendix: RACEMIC ACID, OR PARATARTARIC ACID ($2\,HO, C_8\,H_4\,O_{10}$).

The formula of crystallized racemic acid is $2\,HO, C_8\,H_4\,O_{10} + 2\,aq.$ The crystallization water escapes slowly in the air, but rapidly at 212° F. (difference between racemic acid and tartaric acid). To solvents the racemic acid comports itself like the tartaric acid. The racemates also show very similar deportment to that of the tartrates. However, many of them differ in the amount of water they contain, in form and solubility from the corresponding tartrates. *Chloride of calcium* precipitates from the solutions of free racemic acid and of racemates RACEMATE OF LIME ($2\,CaO, C_8\,H_4\,O_{10} + 8\,aq.$), as a white crystalline powder. Ammonia throws the precipitate down from its solution in hydrochloric acid, either immediately or at least very speedily (difference between racemic acid and tartaric acid). It dissolves in solution of soda and potassa, but is reprecipitated from this solution by boiling (difference between racemic acid and oxalic acid). *Lime-water* added in excess, produces immediately a white precipitate insoluble in chloride of ammonium (difference between racemic acid and tartaric acid). *Solution of sulphate of lime* does not immediately produce a precipitate in a solution of racemic acid (difference between racemic acid and oxalic acid); however, after ten or fifteen minutes racemate of lime separates (difference between racemic acid and tartaric acid); in solutions of neutral racemates the precipitate forms immediately. With *salts of potassa* racemic acid comports itself like tartaric acid.

SECOND GROUP OF THE ORGANIC ACIDS.

ACIDS WHICH CHLORIDE OF CALCIUM FAILS TO PRECIPITATE UNDER ANY CIRCUMSTANCES, BUT WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY SESQUICHLORIDE OF IRON: *Succinic Acid, Benzoic Acid.*

§ 167.

a. SUCCINIC ACID ($2\,HO, C_8\,H_4\,O_6$).

1. Hydrate of Succinic acid forms colorless and inodorous prisms or tables of slightly acid taste, which are readily soluble in water, alcohol, and ether, difficultly soluble in nitric acid, and volatilize when exposed to the action of heat, leaving only a little charcoal behind. The officinal acid has an empyreumatic odor, and leaves a somewhat larger carbonaceous residue upon volatilization. Succinic acid is not destroyed by heating with nitric acid, and may therefore be easily obtained in the pure state by boiling with that acid for half an hour, by which means the oil of amber, if present, will be destroyed. By sublimation crystalline

needles of silky lustre are obtained; the hydrate loses water in this process, so that by repeated sublimation anhydrous acid is ultimately obtained. Heated in the air, succinic acid burns with a blue flame, free from soot.

2. The succinates are decomposed at a red heat; those which have an alkali or alkaline earth for base, are converted into carbonates in this process, the change being attended with separation of charcoal. Most of the succinates are soluble in water.

3. *Sesquichloride of iron* produces in solutions of neutral succinates of the alkalies a brownish pale red, bulky precipitate of SUCCINATE OF SESQUIOXIDE OF IRON ($Fe_2 O_3, C_8 H_4 O_6$); one-third of the succinic acid is liberated in this reaction, and retains part of the precipitate in solution, if the fluid is filtered off hot. The precipitate dissolves readily in mineral acids; ammonia decomposes it, causing the separation of a less bulky precipitate of a highly basic succinate of sesquioxide of iron, and combining with the greater portion of the acid to succinate of ammonia, which dissolves.

4. *Acetate of lead* gives with succinic acid a white precipitate of neutral SUCCINATE OF LEAD ($2 Pb O, C_8 H_4 O_6$), which is very sparingly soluble in water, acetic acid, and succinic acid, but dissolves readily in solution of acetate of lead and in nitric acid. Treated with ammonia, the neutral succinate of lead is converted into a basic salt ($6 Pb O, C_8 H_4 O_6$).

5. A mixture of *alcohol, ammonia,* and *solution of chloride of barium* produces in solutions of free succinic acid and of succinates a white precipitate of SUCCINATE OF BARYTA ($2 Ba O, C_8 H_4 O_6$).

6. *Nitrate of suboxide of mercury* and *nitrate of silver* also precipitate the succinates; the precipitates, however, are not possessed of any characteristic properties.

§ 168.

b. BENZOIC ACID ($H O, C_{14} H_5 O_3$).

1. Pure hydrate of benzoic acid forms inodorous white scales or needles, or simply a crystalline powder. When heated, it fuses, and afterwards volatilizes completely. The fumes of benzoic acid cause a peculiar irritating sensation in the throat, and provoke coughing; when cautiously cooled, they condense to brilliant needles, when kindled, they burn with a luminous sooty flame. The common officinal hydrate of benzoic acid has the odor of benzoin, and leaves a small carbonaceous residue upon volatilization. Hydrate of benzoic acid is very sparingly soluble in cold water, but it dissolves pretty readily in hot water and in alcohol. Addition of water, therefore, imparts a milky turbidity to a saturated solution of benzoic acid in alcohol.

2. Most of the benzoates are soluble in water; only those with weak bases, *e. g.*, sesquioxide of iron, are insoluble. The soluble benzoates have a peculiar, pungent taste. The addition of a *strong acid* to aqueous solutions of benzoates displaces the benzoic acid, which separates as hydrate in the form of a dazzling white, sparingly soluble powder. Benzoic acid is expelled in the same way from the insoluble benzoates, by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. *Sesquichloride of iron* precipitates solutions of free benzoic acid incompletely; solutions of neutral benzoates of the alkalies completely. The precipitate of BENZOATE OF SESQUIOXIDE OF IRON ($2\ Fe_2O_3$, $3\ [C_{14}H_5O_3] + 15$ aq.), is bulky, flesh-colored, insoluble in water. It is decomposed by ammonia in the same manner as succinate of sesquioxide of iron, from which salt it differs in this, that it dissolves in a little hydrochloric acid, with separation of the greater portion of the benzoic acid.

4. *Acetate of lead* fails to precipitate free benzoic acid and benzoate of ammonia, at least immediately; but it produces white, flocculent precipitates in solutions of benzoates with a fixed alkaline base.

5. A mixture of *alcohol, ammonia,* and *solution of chloride of barium* produces NO precipitate in solutions of free benzoic acid or of the alkaline benzoates.

§ 169.

Recapitulation and remarks.—Succinic and benzoic acids are distinguished from all other acids by the facility with which they may be sublimed, and by their deportment with sesquichloride of iron. They are distinguished from one another by the different color of their salts with sesquioxide of iron, and also by their different deportment with chloride of barium and alcohol; but principally by their different degrees of solubility, succinic acid being readily soluble in water, whilst benzoic acid is very difficult of solution. Succinic acid is seldom perfectly pure, and may therefore often be detected by the odor of oil of amber which it emits.

The detection of the two acids, when present in the same solution with other acids, may be effected as follows: precipitate with sesquichloride of iron, warm the washed precipitate with ammonia, filter, concentrate the solution, divide it into two parts, and mix one part with hydrochloric acid, the other with chloride of barium and alcohol.

Succinic acid and benzoic acid do not prevent the precipitation of sesquioxide of iron, alumina, &c., by alkalies.

THIRD GROUP OF THE ORGANIC ACIDS.

ACIDS WHICH ARE NOT PRECIPITATED BY CHLORIDE OF CALCIUM NOR BY SESQUICHLORIDE OF IRON: *Acetic Acid, Formic Acid.*

§ 170.

a. ACETIC ACID ($HO, C_4H_3O_3$).

1. The hydrate of acetic acid forms transparent crystalline scales, which fuse at 62·6° F. to a colorless fluid of a peculiar pungent and penetrating odor, and exceedingly acid taste. When exposed to the action of heat, it volatilizes completely, forming pungent inflammable vapors, which burn with a blue flame. It is miscible with water in all proportions; it is to such mixtures of the acid with water that the name of acetic

acid is commonly applied. The hydrate of acetic acid is also soluble in alcohol.

2. The acetates undergo decomposition at a red heat; among the products of this decomposition we generally find hydrate of acetic acid, and almost invariably acetone ($C_6 H_6 O_2$). The acetates of the alkalies and alkaline earths are converted into carbonates in this process; of the acetates with metallic bases many leave the metal behind in the pure state, others in the form of oxide. Most of the residues which the acetates leave upon ignition are carbonaceous. Nearly all acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are difficult of solution in that menstruum. If acetates are distilled with dilute sulphuric acid, the free acetic acid is obtained in the distillate.

3. If *sesquichloride of iron* is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with sesquichloride of iron, the fluid acquires a deep dark red color, owing to the formation of ACETATE OF SESQUIOXIDE OF IRON. Upon boiling, the fluid becomes colorless if it contains an excess of acetate, the whole of the sesquioxide of iron precipitating as a basic acetate, in the form of brown-yellow flakes. Ammonia precipitates from it the whole of the sesquioxide of iron as hydrate. Upon addition of hydrochloric acid, a fluid which appears red from the presence of acetate of sesquioxide of iron turns yellow (difference from sulphocyanide of iron).

4. Neutral acetates (but not free acetic acid) give with *nitrate of silver* white, crystalline precipitates of ACETATE OF SILVER ($Ag\,O, C_4 H_3 O_3$), which are very sparingly soluble in cold water. They dissolve more easily in hot water, but separate again upon cooling, in the form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

5. *Nitrate of suboxide of mercury* produces in solutions of acetic acid, and more readily still in solutions of acetates, white, scaly crystalline precipitates of ACETATE OF SUBOXIDE OF MERCURY ($Hg_2 O, C_4 H_3 O_3$), which are sparingly soluble in water and acetic acid in the cold, but dissolve without difficulty in an excess of the precipitant. The precipitates dissolve in water upon heating, but separate again upon cooling, in the form of small crystals; in this process the salt undergoes partial decomposition: a portion of the mercury separates in the metallic state, and imparts a gray color to the precipitate. If the acetate of suboxide of mercury is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. When acetates are heated with *concentrated sulphuric acid*, HYDRATE OF ACETIC ACID is evolved, which may be known by its pungent odor. But if the acetates are heated with a mixture of about equal volumes of *concentrated sulphuric acid* and *alcohol*, ACETIC ETHER ($C_4 H_5 O, C_4 H_3 O_3$) is formed. The odor of this ether is highly characteristic and agreeable; it is most distinct upon shaking the mixture when somewhat cooled, and is much less liable to lead to mistakes than the pungent odor of the free acetic acid.

7. If acetates are distilled with dilute sulphuric acid, and the distillate is digested with an excess of oxide of lead, part of the latter dissolves as basic acetate of lead, which may be readily recognised by its alkaline reaction.

§ 171.

b. FORMIC ACID (HO, C_2HO_3).

1. The hydrate of formic acid is a transparent, colorless, slightly fuming liquid, of a characteristic and exceedingly penetrating odor. When cooled to below 32° F., it crystallizes in colorless plates. It is miscible in all proportions with water and with alcohol. When exposed to the action of heat, it volatilizes completely; the vapors are inflammable and burn with a blue flame.

2. The formates, like the corresponding acetates, leave upon ignition either carbonates, oxides, or metals behind, the process being attended with separation of charcoal, and escape of carbide of hydrogen, carbonic acid, and water. All the compounds of formic acid with bases are soluble in water; alcohol likewise dissolves some of them.

3. Formic acid presents the same deportment with *sesquichloride of iron* as acetic acid.

4. *Nitrate of silver* fails to precipitate free formic acid, and decomposes the alkaline formates only in concentrated solutions. The white, sparingly soluble, crystalline precipitate of FORMATE OF SILVER (AgO, C_2HO_3) acquires very rapidly a darker tint, owing to the separation of metallic silver. Complete reduction of the oxide of silver to the metallic state takes place, even in the cold, after the lapse of some time; but immediately, upon applying heat to the fluid containing the precipitated formate of silver. The same reduction of the oxide of silver to the metallic state takes place in a solution of free formic acid, and also in solutions of formates so dilute that the addition of the nitrate of silver failed to produce a precipitate in them. But it does not take place in presence of an excess of ammonia. The rationale of this reduction is as follows: the formic acid, which may be looked upon as a compound of carbonic oxide with water, deprives the oxide of silver of its oxygen, thus causing the formation of carbonic acid, which escapes, and of water, whilst the reduced silver separates in the metallic state.

5. *Nitrate of suboxide of mercury* gives no precipitate with free formic acid; but in concentrated solutions of alkaline formates this reagent produces a white, sparingly soluble precipitate of FORMATE OF SUBOXIDE OF MERCURY (Hg_2O, C_2HO_3), which rapidly becomes gray, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time, but is immediate upon application of heat. This reduction is also attended with the formation of carbonic acid and water, and takes place, the same as with the oxide of silver, both in solutions of free formic acid and in fluids so highly dilute that the formate of suboxide of mercury is retained in solution.

6. If formic acid or an alkaline formate is heated with *chloride of mercury* to from 140° to 158° F., SUBCHLORIDE OF MERCURY precipitates. If the mixture is heated to 212° F., metallic mercury separates along with the subchloride.

7. If formic acid or a formate is heated with *concentrated sulphuric acid*, the formic acid is resolved into water and carbonic oxide gas, which latter escapes with effervescence, and if kindled, burns with a blue flame. The fluid does not turn black in this process. The rationale of the decomposition of the formic acid is this: the sulphuric acid withdraws from the formic acid the water or the oxide necessary for the existence

of the latter acid, and thus occasions a transposition of its elements ($C_2HO_3 = 2CO + HO$). Upon heating formates with dilute sulphuric acid in a distilling apparatus, free formic acid is obtained in the distillate, and may mostly be readily detected by its odor. Upon heating a formate with a mixture of sulphuric acid and alcohol, formic ether is evolved, which is characterized by its peculiar arrack-like smell.

8. If dilute formic acid is heated with *oxide of lead*, the latter dissolves. On cooling the solution, which, if necessary, is concentrated by evaporation, the FORMATE OF LEAD (PbO, C_2HO_3) separates in brilliant prisms or needles.

§ 172.

Recapitulation and remarks.—Acetic acid and formic acid may be distilled over with water, and form with sesquioxide of iron soluble neutral salts which dissolve in water, imparting to the fluid a blood-red color, and are decomposed upon boiling. These reactions distinguish the two acids of the third group from the other organic acids. From each other the two acids are distinguished by the odor of their hydrates and ethyle compounds, and by their different deportment with salts of silver and salts of mercury, oxide of lead, and concentrated sulphuric acid. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of oxide of mercury or oxide of silver. Formic acid reduces the oxides, and suffers decomposition, being resolved into carbonic oxide and water; whilst the acetic acid combines with the oxides, forming acetates, which remain in solution.

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

PART II.

PRELIMINARY REMARKS

ON THE

COURSE OF QUALITATIVE ANALYSIS IN GENERAL AND ON THE PLAN OF THIS PART OF THE PRESENT WORK IN PARTICULAR.

The knowledge of reagents and of the deportment of other bodies with them enables us to ascertain at once whether a compound of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. Thus, for instance, a few simple reactions suffice to show whether a body which appears to be calcareous spar, is really carbonate of lime, and that another, which we hold to be gypsum, *is* actually sulphate of lime. This knowledge usually suffices also to ascertain whether a certain body is present or not in a compound; for instance, whether or not a white powder contains subchloride of mercury. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover *all* the constituents of a mixture or chemical compound—if we intend to prove that, besides certain bodies which we have detected in a mixture or compound, no other substance *can* possibly be present—if consequently a *complete qualitative analysis* is our object, the mere knowledge of the reagents, and of the reactions of other bodies with them, will not suffice for the attainment of this end; this requires the additional knowledge of a systematic and progressive course of analysis, in other words, the knowledge of the *order* and *succession* in which solvents, and general and special reagents, should be applied, both to effect the speedy and certain detection of every component element of a compound or mixture, and to prove with certainty the absence of all other substances. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method whatever in our investigations and experiments, analyzing becomes (at least in the hands of a novice) mere guess work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances present or supposed to be present in a

compound or mixture, are in the first place classed into certain groups, which are then again subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order and succession in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a certain definite course, or system, of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will in certain given cases most readily and rapidly lead to the attainment of the object in view.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining simplicity with the greatest possible security, is the object of the *First Section* of the second part of this work.

The elements and compounds comprised in it are the same which we have studied in Part I., with the exception of those given in that part simply by way of appendix.

The *First Section* of the Second Part consists of PRACTICAL INSTRUCTIONS IN ANALYSIS, wherein I have laid down a systematic course which, with due care and attention, will, by progressive steps, lead speedily and safely to the attainment of the end in view.

The subdivisions of this practical course are, 1, Preliminary examinations; 2, Solution; 3, Actual examination.

The third subdivision (the *actual examination*) is again subdivided into, (1) Examination of compounds in which but one base and one acid are assumed to be present; and, (2) Examination of mixtures or compounds in which all the substances treated of in the present work are assumed to be present. With respect to the latter section, I have to remark that where the preliminary examination has not clearly demonstrated the absence of certain groups of substances, the student cannot safely disregard any of the paragraphs to which reference is made in consequence of the reactions observed. In cases where the intention is simply to test a compound or mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular numbers which ought to be attended to.

As the construction of a universally applicable systematic course of analysis requires due regard to, and provision for, every contingency that may possibly arise, it is self-evident that, though in the system here laid down the various bodies comprised in it have been assumed to be mixed up together in every conceivable way, it was absolutely indispensable to proceed throughout upon the supposition that no foreign organic matters whatever were present, since the presence of such matters would of course tend to prevent or obscure many reactions, and variously modify others.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, with a very few exceptions, still there are special cases in which it may be advisable to modify it. A preliminary treatment of the substance is also sometimes necessary, before the actual analysis can be proceeded with; the presence of coloring, slimy, organic matters more especially requires certain preliminary operations.

The *Second Section* of this Part will be found to contain a detailed description of the special methods employed to effect the analysis of a few important compounds and mixtures which chemists are frequently called upon to examine. Some of these methods show how the analytical processes become simplified as the number of substances decreases to which regard must be had in the analysis.

In conclusion, as an intelligent and successful pursuit of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of bodies depend, since this knowledge alone can furnish the student with a guide to the selection of the proper reagents, and the order in which they ought to be applied, I have given in the *Third Section* of the Second Part an explanation and elucidation of the general analytical process, with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second sections, I strongly recommend students to make themselves early and thoroughly acquainted with it. I have devoted a special section to this theoretical explanation of the process, as I think it will be understood better in a connected form, than it would have been by explanatory additions to several paragraphs, which, moreover, might have materially interfered with the plainness and perspicuity of the plan of the practical process.

SECTION I.

PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

I. Preliminary Examination.*

§ 173.

1. Examine, in the first place, the physical properties—color, shape, hardness, gravity, odor, &c.—of the substance intended for analysis, since these will often enable you in some measure to infer its nature. Before proceeding to the application of any chemical process, you must always consider how much of the substance to be analyzed you have at command, since it is necessary, at this early period of the examination, to calculate the quantity which may safely be used in the preliminary investigation. A reasonable economy is in all cases advisable, even though you may possess the substance in large quantities; but, under all circumstances, let it be a fixed rule, never to use at once the whole of what you possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments. 1†

* Consult also the observations and additions in the Third Section.

† These marginal numbers are simply intended to facilitate reference.

A. The Body under Examination is Solid.

I. It is neither a Pure Metal nor an Alloy.

§ 174.

1. The substance is fit for examination if in powder or in minute crystals; but if in larger crystals or in solid pieces, it is necessary in the first place to reduce a portion of it to powder if practicable. Bodies of the softer kind may be triturated in a porcelain mortar; those of a harder nature must first be broken into small pieces in a steel mortar, or upon a steel anvil, and the pieces then be triturated in an agate mortar. 2

2. Put some of the powder into a glass tube, sealed at one end, about six centimètres long and five millimètres wide, and heat first gently over the spirit or gas-lamp, then intensely in the blowpipe flame. The reactions resulting may lead to many positive or probable conclusions regarding the nature of the substance. The following are the most important of these reactions, to which particular attention ought to be paid; it often occurs that several of them are observed in the case of one and the same substance. 3

a. THE SUBSTANCE REMAINS UNALTERED: absence of organic matters, salts containing water of crystallization, readily fusible matters, and volatile bodies. 4

b. THE SUBSTANCE DOES NOT FUSE AT A MODERATE HEAT, BUT SIMPLY CHANGES COLOR. From white to yellow, turning white again on cooling, indicates OXIDE OF ZINC; from white to yellowish-brown, turning to a dirty light yellow on cooling, indicates BINOXIDE OF TIN; if the color changes from white to brownish-red, turning to yellow on cooling, and the body is fusible at a red heat, this indicates the presence of OXIDE OF LEAD; if the color changes from white to orange-yellow, or a deeper and more reddish tint, up to reddish-brown, turning pale yellow on cooling, and the body fuses at an intense red heat, this indicates the presence of TEROXIDE OF BISMUTH; if the color changes from red to black, turning red again on cooling, this indicates the presence of SESQUIOXIDE OF IRON, &c. 5

c. THE SUBSTANCE FUSES WITHOUT EXPULSION OF AQUEOUS VAPOR. If on intense heating, gas (oxygen) is evolved, and a small fragment of charcoal thrown in is energetically consumed, NITRATES or CHLORATES may be assumed to be present. 6

d. AQUEOUS VAPORS ARE EXPELLED, WHICH CONDENSE IN THE COLDER PART OF THE TUBE: this indicates the presence either (α) of SUBSTANCES CONTAINING WATER OF CRYSTALLIZATION, in which case they will generally readily fuse, and re-solidify after expulsion of the water; many of these swell considerably whilst yielding up their water, *e. g.* (borax, alum); or (β) of decomposable HYDRATES, in which case the bodies often will not fuse; or (γ) of anhydrous salts, holding water mechanically enclosed between their lamellæ—in which case the bodies will decrepitate; or (δ) of bodies with moisture externally adhering to them. 7

Test the reaction of the condensed fluid in the tube: if it is alkaline, ammonia may be assumed to be present; if acid, a volatile acid (sulphuric acid, sulphurous acid, hydrofluoric acid, hydrochloric, hydrobromic, or hydriodic acids, nitric acid, &c.).

e. GASES OR FUMES ESCAPE. Observe whether they have a color, smell, acid or alkaline reaction, whether they are inflammable, &c. 8

aa. OXYGEN. The disengagement of this gas indicates the presence of peroxides, chlorates, nitrates, &c. A glimmering slip of wood is relighted in the gaseous current.

bb. SULPHUROUS ACID. This is often produced by the decomposition of sulphates; it may be known by its peculiar odor and by its acid reaction.

cc. HYPONITRIC ACID, resulting from the decomposition of nitrates, especially with oxides of the heavy metals; it may be known by the brownish-red color of the fumes.

dd. CARBONIC ACID. The evolution of carbonic acid indicates the presence of carbonates decomposable by heat. The gas evolved is colorless and tasteless, non-inflammable; a drop of lime-water on a watch-glass becomes turbid on exposure to the gaseous current.

ee. CARBONIC OXIDE GAS. The escape of this gas indicates the presence of oxalates, and, when attended with actual carbonization, also of formates. The gas burns with a blue flame.

ff. CYANOGEN. The evolution of cyanogen gas denotes the presence of cyanides decomposable by heat. The gas may be known by its odor, and the crimson flame with which it burns.

gg. HYDROSULPHURIC ACID GAS. The escape of hydrosulphuric acid gas indicates the presence of sulphides containing water; the gas may be readily known by its odor.

hh. AMMONIA, resulting from the decomposition of ammoniacal salts, or also of cyanides or nitrogenous organic matters, in which latter cases browning or carbonization of the substance takes place, and either cyanogen or offensive empyreumatic oils escape with the ammonia.

f. A SUBLIMATE FORMS. This indicates the presence of volatile bodies: the following are those more frequently met with:— 9

aa. SULPHUR. Separated from mixtures or from many of the metallic sulphides. Sublimes in reddish-brown drops which become solid on cooling, and turn yellow, or yellowish-brown.

bb. AMMONIA SALTS give white sublimates; heated with soda and a drop of water on platinum foil, they evolve ammonia.

cc. MERCURY and compounds of mercury. METALLIC MERCURY forms globules; SULPHIDE OF MERCURY is black, but acquires a red tint when rubbed; CHLORIDE OF MERCURY fuses before volatilizing; SUBCHLORIDE OF MERCURY sublimes

without previous fusion; the sublimate, which is yellow whilst hot, turns white on cooling. The red IODIDE OF MERCURY gives a yellow sublimate.

dd. ARSENIC and compounds of that metal. METALLIC ARSENIC forms the well-known arsenical mirror; ARSENIOUS ACID forms small shining crystals; the SULPHIDES OF ARSENIC give sublimates which are reddish-yellow whilst hot, and turn yellow on cooling.

ee. TEROXIDE OF ANTIMONY fuses to a yellow liquid before subliming. The sublimate consists of brilliant needles.

ff. BENZOIC ACID and SUCCINIC ACID, which may be known by the odor of their fumes.

gg. HYDRATED OXALIC ACID. White crystalline sublimate, thick fumes in the tube. Heating a small sample on platinum foil with a drop of concentrated sulphuric acid gives rise to a copious evolution of gas.

g. CARBONIZATION TAKES PLACE: organic substances. This 10
is always attended with evolution of gases (in the case of acetates of acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with alkalies or alkaline earths.

3. Put a small portion of the substance on a charcoal support (in 11
the cavity scooped out for the purpose), and expose to the inner blowpipe flame.

As most of the reactions described under 2 (3—10) are also produced by this process, I will here enumerate only those which result more particularly and exclusively from its application.

a. THE BODY FUSES, AND IS ABSORBED BY THE CHARCOAL OR 12
FORMS A BEAD IN THE CAVITY: this denotes more particularly the presence of salts of the alkalies.

b. AN INFUSIBLE WHITE RESIDUE REMAINS on the charcoal, 13
either at once or after previous melting in the water of crystallization. This indicates more particularly the presence of baryta, strontia, lime, magnesia, alumina, oxide of zinc (which appears yellow whilst hot), and silicic acid. Among these substances, STRONTIA, LIME, MAGNESIA, and OXIDE OF ZINC, are distinguished by strong luminosity in the blowpipe flame. Moisten the white residue with a drop of solution of nitrate of protoxide of cobalt, and expose again to a strong heat. If the mass assumes a fine blue tint, this indicates the presence of ALUMINA; if a reddish tint, of MAGNESIA; if a green color, of OXIDE OF ZINC. If SILICIC ACID is present, the mass also assumes a faint bluish tint, which must not be confounded with that proceeding from the presence of alumina.

c. THE SUBSTANCE LEAVES AN INFUSIBLE RESIDUE OF 14
ANOTHER COLOR, OR REDUCTION TO THE METALLIC STATE TAKES PLACE, WITH OR WITHOUT INCRUSTATION OF THE CHARCOAL. Mix a portion of the powder with carbonate of soda, and heat on charcoal in the reducing flame; observe the residue in the cavity, as well as the incrustation on the charcoal.

α. The sustained application of a strong flame produces a me- 15
tallic globule, without incrustation of the charcoal; this indi-

cates the presence of GOLD, SILVER, or COPPER. The oxides of platinum, iron, cobalt, and nickel, are indeed also reduced, but they yield no metallic globules.

β. The charcoal support is coated with an incrustation, either with or without simultaneous formation of a metallic globule. 16

aa. The incrustation is *white*, at a long distance from the test specimen, and is very readily dissipated by heat, emitting a garlic-like odor: ARSENIC.

bb. The incrustation is *white*, is nearer the test specimen than in *aa*, and may be driven from one part of the support to another: ANTIMONY. Metallic globules are generally observed at the same time, which continue to evolve white fumes long after the blowpipe jet is discontinued, and upon cooling become surrounded with crystals of teroxide of antimony; the globules are brittle.

cc. The incrustation is *yellow* whilst hot, but turns white on cooling; it is near the test specimen, and is with difficulty volatilized: ZINC.

dd. The incrustation has a *faint yellow* tint whilst hot, but turns white on cooling; it surrounds the test specimen, and both the inner and outer flame fail to volatilize it: TIN. The metallic globules formed at the same time are bright, readily fusible, and malleable.

ee. The incrustation has a *lemon-yellow* color, turning on cooling to sulphur-yellow; when exposed to the reducing flame, it leaves a bluish stain: LEAD. Readily fusible, malleable globules are formed at the same time with the incrustation.

ff. The incrustation is of a *dark orange-yellow* color whilst hot, which changes to lemon-yellow on cooling; when exposed to the reducing flame, it does not leave a bluish stain: BISMUTH. The metallic globules formed at the same time as the incrustation are readily fusible and brittle.

gg. The incrustation is reddish-brown, in thin layers, orange-yellow; it volatilizes without leaving a colored stain: CADMIUM.

4. Fuse a small portion together with a bead of microcosmic salt, and expose for some time to the outer flame of the blowpipe. 17

a. THE SUBSTANCE DISSOLVES READILY AND RATHER LARGELY TO A CLEAR BEAD (WHILST HOT).

a. *The hot bead is colored:* 18

BLUE, by candlelight inclining to violet—COBALT;

GREEN, upon cooling blue; in the reducing flame, after cooling, red—COPPER;

GREEN, particularly fine on cooling, unaltered in the reducing flame—CHROMIUM;

BROWNISH-RED, on cooling light yellow or colorless; in the reducing flame red whilst hot, yellow whilst cooling, then greenish—IRON;

DARK YELLOW to REDDISH, turning lighter or altogether colorless on cooling; in the reducing flame unaltered—NICKEL;

YELLOWISH-BROWN, on cooling changing to light yellow or losing its color altogether; in the reducing flame almost colorless (especially after contact with tin), blackish-gray on cooling—BISMUTH;

BRIGHT YELLOWISH to OPAL, when cold rather dull; in the reducing flame whitish-gray—SILVER;

AMETHYST-RED, especially on cooling; colorless in the reducing flame, not quite clear—MANGANESE.

β. The hot bead is colorless: 19

IT REMAINS CLEAR ON COOLING: ANTIMONY, ALUMINA, ZINC, CADMIUM, LEAD, LIME, MAGNESIA; the latter five metals, when added in somewhat large proportion to the microcosmic salt, give enamel-white beads; the bead of oxide of lead is yellowish when saturated;

IT BECOMES ENAMEL-WHITE ON COOLING, even when only a small portion of the powder has been added to the microcosmic salt: BARYTA, STRONTIA.

b. THE SUBSTANCE DISSOLVES SLOWLY AND ONLY IN SMALL QUANTITY: 20

α. The bead is colorless, and remains so even after cooling; the undissolved portion looks semi-transparent; upon addition of a little sesquioxide of iron, it acquires the characteristic color of an iron bead: SILICIC ACID.

β. The bead is colorless, and remains so after addition of a little sesquioxide of iron: TIN.

c. THE SUBSTANCE DOES NOT DISSOLVE, BUT FLOATS (IN THE METALLIC STATE) IN THE BEAD: GOLD, PLATINUM. 21

As the body under examination may consist of a mixture of the most dissimilar elements, it is impossible to give well defined cases that shall offer at the same time the advantage of general applicability. If, therefore, reactions are observed in an experiment which proceed from a combination of two or several cases, the conclusions drawn from these reactions must of course be modified accordingly.

§ 175.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. Heat a small portion of the substance with water acidulated with acetic acid. 22

a. HYDROGEN GAS IS EVOLVED: this indicates the presence of a light metal (possibly also of manganese in the metallic state). The presence of alkalies and of alkaline earths must also be had regard to in the actual examination.

b. NO HYDROGEN IS EVOLVED: this indicates the absence of light metals. Alkalies and alkaline earths may be altogether disregarded in the course of the special investigation.

2. Heat a sample of the substance on charcoal in the reducing flame of the blowpipe, and watch the reactions; for instance, whether the substance fuses, whether an incrustation is formed, or an odor emitted, &c. 23

a. THE SAMPLE REMAINS UNALTERED: this is pretty conclusive

of the absence of antimony, zinc, lead, bismuth, cadmium, tin, mercury, and arsenic; the absence of gold, silver, and copper is also probable; PLATINUM, IRON, MANGANESE, NICKEL, and COBALT are likely to be present.

b. THE SAMPLE FUSES; NO INCRUSTATION FORMS, AND NO ODOR IS EMITTED: absence of antimony, zinc, lead, bismuth, cadmium, and arsenic; presence of GOLD, SILVER, COPPER.

c. THE SAMPLE FUSES, AND AN INCRUSTATION IS FORMED, BUT NO ODOR EMITTED: absence of arsenic, and presence of ANTIMONY, ZINC, BISMUTH, LEAD, CADMIUM (compare § 174, 3, *c*, β [16]).

d. THE SUBSTANCE EMITS THE ODOR OF GARLIC; ARSENIC is present. According to the nature of the other reactions which may manifest themselves, *a*, *b*, or *c* must be had regard to.

3. Heat a sample of the substance before the blowpipe in a glass tube sealed at one end. 24

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE: absence of mercury.

b. A SUBLIMATE IS FORMED; presence of MERCURY, CADMIUM, or ARSENIC. The sublimate of mercury, which consists of small globules, cannot possibly be confounded with that of cadmium or arsenic.

§ 176.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. Evaporate a small portion of the fluid in a platinum dish, or in a small porcelain crucible, to ascertain whether it actually contains any matter in solution; if a residue remains, examine this as directed § 174. 25

2. Test with litmus paper (blue and red). 26

a. THE FLUID REDDENS BLUE LITMUS PAPER. This reaction may be caused by a free acid or an acid salt, as well as by a metallic salt soluble in water. To distinguish between these two cases, pour a small quantity of the fluid into a watch-glass, and dip into it a small glass rod, the extreme point of which has previously been moistened with dilute solution of carbonate of soda; if the fluid remains clear, or if the precipitate which may form at first, redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble metallic salt. As a matter of course, a solution which contains a free acid or an acid salt can no longer be considered simply aqueous, and the subsequent examination must accordingly be conducted with due regard to the possible presence of substances insoluble in water but soluble in acids.

b. REDDENED LITMUS PAPER TURNS BLUE: this indicates the presence of free alkalies or alkaline carbonates, free alkaline earths, alkaline sulphides, and of a number of other salts which show this reaction. In presence of a free alkali, a body dissolved in a fluid is as likely to belong to the class of substances soluble, as to that of bodies insoluble in water. For 27

the way to settle this point, and also for further information on the subject of alkaline solutions in general, I refer to § 187, I. 2 (**104**).

3. Smell the fluid or, should this fail to give satisfactory results, distil, to ascertain whether the simple solvent present is water, alcohol, ether, &c. If you find it is not water, evaporate the solution to dryness, and treat the residue as directed § 174. **28**

4. If the solution is aqueous, and manifests an acid reaction, dilute a portion of it largely with water. Should this impart a milky and turbid appearance to it, the presence of ANTIMONY, BISMUTH (possibly also of tin) may be inferred. If the precipitate disappears upon the addition of tartaric acid, there is reason to believe it consists of antimony; if it is not redissolved by tartaric acid, but by nitric acid, you may assume the presence of bismuth. Treat the original fluid either as directed § 180 or as directed § 187, according as you have reason to suppose it to be the solution of a simple or a compound (mixed) substance. **29**

II. Solution of Bodies, or Classification of Substances according to their Deportment with Certain Solvents.*

§ 177.

Water, hydrochloric or nitric acid, and aqua regia are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective behavior with these solvents. **30**

First class.—SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

Third class.—SUBSTANCES INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER AS WELL AS IN HYDROCHLORIC ACID, NITRIC ACID, AND AQUA REGIA.

The solution of alloys being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for these substances (see § 179).

The process of solution is conducted in the following manner.

A. The Substance under Examination is neither a Metal nor an Alloy.

§ 178.

1. Put about a gramme (15·5 grains) of the finely pulverized substance under examination into a small flask or a test-tube, add from ten to twelve times the amount of distilled water, and heat to boiling over a spirit- or gas-lamp. **31**

a. THE SUBSTANCE DISSOLVES COMPLETELY. In that case it belongs to the first class; regard must be had to what has been **32**

* Consult the remarks in the third section.

stated in § 176, 2 (**26**), concerning the reactions with test-papers. Treat the solution either as directed § 180 or as directed § 187, according as either one or several acids and bases are supposed to be present.

b. AN INSOLUBLE RESIDUE REMAINS, EVEN AFTER PROTRACTED BOILING. Let the residue subside, and filter the fluid off, if practicable in such a manner as to retain the residue in the test-tube; evaporate a few drops of the clear filtrate on platinum foil; if nothing remains, the substance is completely insoluble in water; in which case proceed as directed § 178, 2 (**34**). But if a residue remains, the substance is at least partly soluble; in which case boil again with water, filter, add the filtrate to the original solution, and treat the fluid, according to circumstances, either as directed § 180, or according to § 187. Wash the residue with water, and proceed as directed § 178, 2 (**34**). **33**

2. Treat a small portion of the residue which has been boiled with water (**33**) with dilute hydrochloric acid. If it does not dissolve, heat to boiling, and if this fails to effect complete solution, decant the fluid into another test-tube, boil the residue with concentrated hydrochloric acid, and, if it dissolves, add it to the fluid in the other test-tube. The reactions which may manifest themselves in this operation, and which ought to be carefully observed are, (α) Effervescence, which indicates the presence of carbonic acid or hydrosulphuric acid; (β) Evolution of chlorine, which indicates the presence of peroxides, chromates, &c.; (γ) Emission of the odor of hydrocyanic acid, which indicates the presence of insoluble cyanides. The analysis of the latter bodies being effected in a somewhat different manner, a special paragraph will be devoted to them (see § 202). **34**

a. THE RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID (except perhaps that sulphur separates, which may be known by its color and light specific gravity, and may, after boiling some time longer, be removed by filtration; or that gelatinous hydrate of silicic acid separates). Proceed, according to circumstances, either as directed § 183, or as directed § 188, after previous filtration if necessary. The body belongs to the second class. To make quite sure of the actual nature of the sulphur or hydrated silicic acid filtered off, examine these residuary matters as directed § 186, or as directed § 201. **35**

b. THERE IS STILL A RESIDUE LEFT. In that case put aside the test-tube containing the specimen which has been boiled with the hydrochloric acid, and try to dissolve another sample of the substance under examination, by boiling with nitric acid, and subsequent addition of water. **36**

α. *The sample is completely dissolved, or leaves no other residue but sulphur or the gelatinous hydrate of silicic acid;* in this case also the body belongs to the second class. Use this solution to test further for bases, and then proceed as directed in 2, *a* (**35**). **37**

β. *After boiling with nitric acid there is still a residue left.* Pass on to 3. **38**

3. If the residue insoluble in water will not entirely dis- **39**

solve in hydrochloric acid nor n nitric acid, try to effect complete solution of it by means of nitro-hydrochloric acid. To this end mix the contents of the tube treated with nitric acid with the contents of the tube treated with concentrated hydrochloric acid; heat the mixture to boiling, and should this fail to effect complete solution, decant the clear fluid off from the undissolved residue, boil the latter for some time with concentrated nitro-hydrochloric acid, and add the decanted solution in dilute aqua regia as well as the solution in dilute hydrochloric acid decanted in § 178, 2 (**34**). Heat the entire mixture once more to boiling, and observe whether complete solution has now been effected, or whether the action of the concentrated nitro-hydrochloric acid has still left a residue. In the *latter* case, filter the solution—if necessary, after addition of some water*—wash the residue with boiling water, and proceed with the filtrate, and the washings added to it, as directed § 183, or as directed § 188;—in the *former* case, proceed with the clear solution in the same way.†

4. If boiling nitrohydrochloric acid has left an undissolved residue, wash it thoroughly with water, and then proceed as directed § 186, or as directed § 201. **40**

B. The Substance under Examination is a Metal or an Alloy.

§ 179.

The metals are best classed according to their respective behavior with nitric acid: this gives us, **41**

I. Metals which are not attacked by nitric acid: gold, platinum.

II. Metals which are oxidized by nitric acid, but of which the oxides do not dissolve in an excess of the acid nor in water; antimony, tin.

III. Metals which are oxidized by nitric acid and converted into nitrates, which dissolve in an excess of the acid or in water: all other metals.

Pour nitric acid of 1·25 sp. gr. over a small portion of the metal or alloy under examination, and apply heat.

1. Complete solution takes place, either at once or upon addition of water; this proves the absence of platinum,‡ gold, antimony,‖ and tin. Proceed, according to circumstances, either as directed § 183, or as instructed § 187, III. (**109**). **42**

2. A residue is left.

a. A metallic residue. Filter, and treat the filtrate as directed § 187, III., after having examined, in the first place, **43**

* If the fluid turns turbid upon addition of water, this indicates the presence of bismuth or antimony; the turbidity disappears again upon addition of hydrochloric acid.

† If the acid solution on cooling deposits acicular crystals, the latter generally consist of chloride of lead; it is in that case often advisable to decant the fluid off from the crystals, and to examine fluid and crystals separately.

‡ Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

‖ Very minute traces of antimony, however, are often completely dissolved by nitric acid.

whether anything has really been dissolved. Wash the residue thoroughly, dissolve in nitrohydrochloric acid, and add to a portion of the solution chloride of potassium and alcohol; to another portion, sulphate of protoxide of iron; a yellow precipitate in the first indicates the presence of PLATINUM, a black precipitate in the second, the presence of GOLD.

b. A white, pulverulent residue; this indicates the presence of ANTIMONY and TIN. Filter, ascertain whether anything has been dissolved, and if so treat the filtrate as directed § 187, III. Wash the residue thoroughly, and heat it with a hot saturated solution of bitartrate of potassa, or with a solution of tartaric acid. 44

α. Complete solution ensues; this indicates the presence of oxide of ANTIMONY alone; test the solution with hydrosulphuric acid, after addition of some hydrochloric acid. 45

β. A white residue remains, even after boiling with a fresh portion of solution of bitartrate of potassa or tartaric acid; this indicates the probable presence of TIN. Filter and mix the filtrate with some hydrochloric acid, then with solution of hydrosulphuric acid. If an orange-red precipitate is formed, TEROXIDE OF ANTIMONY is present. It is always necessary to ascertain whether the residue consists really of binoxide of tin: which may be known by heating it to redness, then fusing it in a small tube with cyanide of potassium, boiling the reduced metal with water, then heating with hydrochloric acid, and testing the solution with chloride of mercury (§ 133).

III. ACTUAL EXAMINATION.

*Simple Compounds.**

A. SUBSTANCES SOLUBLE IN WATER.

Detection of the Base.†

§ 180.

1. Add some hydrochloric acid to a portion of the aqueous solution. 46

a. NO PRECIPITATE IS FORMED; this is a positive proof of the absence of silver and suboxide of mercury, and is likewise an indication of the probable absence of lead. Pass on to § 180, 2 (50).

b. A PRECIPITATE IS FORMED. Divide the fluid in which the precipitate is suspended into two portions, and add ammonia in excess to the one. 47

α. *The precipitate redissolves, and the fluid becomes clear;* this shows the precipitate to have consisted of chloride of silver, and is consequently indicative of the presence of SILVER.

* This term is used here, and wherever it happens to occur hereafter in the present work, to designate compounds supposed to contain only *one* base and *one* acid, or *one* metal and *one* non-metallic element.

† Arsenious acid and arsenic acid are included here.

To arrive at a positive conviction on this point, the original solution must be tested with chromate of potassa, and with hydrosulphuric acid (see § 114, 4, and § 138, *b*, 6).

β. The precipitate turns black: this shows the precipitate to have consisted of subchloride of mercury, which has now been converted by the ammonia into suboxide of mercury; it is consequently indicative of the presence of SUBOXIDE OF MERCURY. To set all doubt on this point at rest, test the original solution with protochloride of tin, and with metallic copper (see § 115). 48

γ. The precipitate remains unaltered; it consists in that case of chloride of lead, which is not dissolved by ammonia; this reaction is accordingly indicative of the presence of LEAD. Whether the precipitate consists really of chloride of lead or not is conclusively ascertained: 1st, by diluting the second portion of the fluid in which the precipitate produced by hydrochloric acid is suspended, with a large amount of water, and applying heat; the precipitate must dissolve if it consists of chloride of lead; and 2nd, by adding dilute sulphuric acid to the original solution (§ 116, 8). 49

2. Add to the fluid acidified with hydrochloric acid (1) solution of hydrosulphuric acid until it smells distinctly of that gas, even after shaking, and heat the mixture. 50

a. THE FLUID REMAINS CLEAR. Pass on to 3 (**56**), since this is a proof that lead, bismuth, copper, cadmium, oxide of mercury, gold, platinum, tin, antimony, arsenic, and sesquioxide of iron, are not present.

b. A PRECIPITATE IS FORMED.

α. THIS PRECIPITATE IS WHITE; it consists in that case of separated sulphur, and is indicative of the presence of SESQUIOXIDE OF IRON (§ 110, 3). However, as the separation of sulphur may also be caused by other substances, it is indispensable that you should satisfy yourself whether the substance present is really sesquioxide of iron or not. For this purpose test the original solution with ammonia, and with ferrocyanide of potassium (§ 110, 5 and 6). 51

β. THE PRECIPITATE IS YELLOW; in that case it may consist either of sulphide of cadmium, sulphide of arsenic, or bisulphide of tin; it indicates accordingly the presence of either cadmium, arsenic, or binoxide of tin. To distinguish between them, mix a portion of the fluid wherein the precipitate is suspended with ammonia in excess, add some sulphide of ammonium, and heat. 52

aa. The precipitate does not dissolve; it consists of CADMIUM; for sulphide of cadmium is insoluble in ammonia and sulphide of ammonium. The blowpipe is resorted to as a confirmatory test (§ 121, 8).

bb. The precipitate dissolves: BINOXIDE OF TIN OR ARSENIC; add ammonia to a small portion of the original solution.

aa. A white precipitate is formed. BINOXIDE OF TIN is the substance present. Positive conviction is obtained by reducing the precipitate before the blowpipe,

with cyanide of potassium and carbonate of soda (§ 129, 8).

ββ. *No precipitate is formed.* This indicates the presence of ARSENIC. Positive conviction may be arrived at by the production of an arsenical mirror, which is effected by reducing the original substance or the precipitated sulphide of arsenic, either with cyanide of potassium and carbonate of soda, or in some other way; and moreover by exposing the original substance in conjunction with carbonate of soda to the inner flame of the blowpipe (§ 131, 12 and 13). If the solution (50) contained *arsenious* acid, the yellow precipitate (52) formed immediately upon the addition of the hydrosulphuric acid; if *arsenic* acid, it formed only upon the application of heat, or after long standing. For further information respecting the means of distinguishing between the two acids see § 133.

γ. THE PRECIPITATE IS ORANGE-COLORED; in that case it 53
consists of tersulphide of antimony, and indicates the presence of TEROXIDE OF ANTIMONY. For confirmation, the original solution is tested with zinc in a small platinum dish (§ 130, 8).

δ. THE PRECIPITATE IS BROWN. It consists of protosul- 54
phide of tin, and indicates the presence of PROTOXIDE OF TIN. To remove all doubt, test a portion of the original solution with solution of chloride of mercury (§ 128, 8).

ε. THE PRECIPITATE IS BROWNISH-BLACK OR BLACK. It may 55
in that case consist of sulphide of lead, sulphide of copper, tersulphide of bismuth, tersulphide of gold, bisulphide of platinum, or sulphide of mercury. To distinguish between these different sulphides, the following experiments are resorted to.

aa. Add dilute sulphuric acid to a portion of the original solution; if a white precipitate is formed, this indicates LEAD. To dispel all doubt, test with chromate of potassa (§ 116).

bb. Add solution of soda to a portion of the original solution; if a yellow precipitate is formed, this indicates OXIDE OF MERCURY. The reactions with protochloride of tin and metallic copper afford positive certainty on the point (§ 118).

The presence of oxide of mercury is usually sufficiently indicated by the several changes of color through which the precipitate produced by the solution of hydrosulphuric acid in the fluid under examination is observed to pass; this precipitate is white at first, but changes upon the addition of an excess of the precipitant to yellow, then to orange, and finally to black (§ 118, 3).

cc. Add ammonia in excess to a portion of the original solution; if a bluish precipitate is formed which redissolves in an excess of the precipitant, imparting an azure color to the fluid, this indicates COPPER. To remove all doubt, test with ferrocyanide of potassium (§ 119.).

dd. If the precipitate produced by ammonia was white, and excess of ammonia has failed to redissolve it, filter the fluid off, wash the precipitate, dissolve it on a watch-glass in 1 or 2 drops of hydrochloric acid, with addition of 2 drops of water, and then add some more water. If the solution turns turbid and milky, this is caused by basic terchloride of bismuth: the reaction consequently indicates BISMUTH. The blowpipe is resorted to as a conclusive test (§ 120).

ee. Add solution of sulphate of protoxide of iron to a portion of the original solution. The formation of a fine black precipitate is indicative of the presence of GOLD. To remove all doubt as to the nature of the precipitate, expose it to the flame of the blowpipe, or test the original solution with protochloride of tin (§ 125).

ff. Add chloride of potassium and alcohol to a portion of the original solution; the formation of a yellow crystalline precipitate is indicative of the presence of PLATINUM. To remove all doubt, heat the precipitate to redness (§ 126).

3. Mix a small portion of the original solution with chloride of ammonium, add ammonia to alkaline reaction, and then, no matter whether the latter reagent has produced a precipitate or not, a little sulphide of ammonium, and apply heat, if a precipitate fail to separate in the cold. 56

a. NO PRECIPITATE IS FORMED; pass on to § 180, 4 (62); for iron, cobalt, nickel, manganese, zinc, chromium, alumina, and silicic acid, are not present.

b. A PRECIPITATE IS FORMED.

α. The precipitate is black: protoxide of iron, nickel, or cobalt. Mix a portion of the original solution with some solution of potassa or soda. 57

aa. A dirty greenish-white precipitate is formed, which soon changes to reddish-brown, upon exposure to the air: PROTOXIDE OF IRON. To remove all doubt, test with ferricyanide of potassium (§ 109).

bb. A precipitate of a light greenish tint is produced, which does not change color: NICKEL. The reaction with ammonia, and the precipitation of the ammoniacal solution by potassa or soda, will afford positive certainty on the point (§ 107).

cc. A sky-blue precipitate is formed, which is discolored upon boiling, and acquires a dark tint: COBALT. The blowpipe is resorted to as a conclusive test (§ 108).

β. The precipitate is not black. 58

aa. If the precipitate is distinctly flesh-colored, it consists of sulphide of manganese, and is consequently indicative of the presence of PROTOXIDE OF MANGANESE. To remove all doubt, add soda to the original solution, or try before the blowpipe (§ 106).

bb. If the precipitate is bluish-green, it consists of hydrated sesquioxide of chromium, and is consequently indicative of the presence of SESQUIOXIDE OF CHROMIUM. To

dispel all doubt, test the original solution with soda, and apply the blowpipe tests (§ 101).

cc. If the precipitate is white, it may consist of hydrate of alumina, or hydrate of silicic acid, or sulphide of zinc, and may accordingly point to the presence of either alumina or oxide of zinc or silicic acid; the latter, in that case, is generally contained in the original solution as an alkaline silicate. To distinguish between these three bodies, add to a portion of the original solution a drop of solution of soda, wait to see whether this produces a precipitate, and then add some more solution of soda, until the precipitate formed is redissolved. 59

aa. If solution of soda fails to produce a precipitate, there is reason to test for SILICIC ACID. For that purpose, evaporate a portion of the original solution with hydrochloric acid to dryness, and treat the residue with hydrochloric acid and water (§ 150, 2), when the silicic acid will be left undissolved. Determine the nature of the alkali which has been dissolved, as directed § 180, 6, *b* (66). 60

ββ. If solution of soda produces a precipitate, which redissolves in an excess of the precipitant, add to a portion of this alkaline fluid hydrosulphuric acid; the formation of a white precipitate indicates the presence of ZINC. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 105). If hydrosulphuric acid fails to produce a precipitate, add to the remaining portion of the alkaline fluid chloride of ammonium, and apply heat. The formation of a white precipitate indicates the presence of ALUMINA. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 100).

Note to § 180, 3, *b*, *β* (58).

As very slight contaminations may impair the distinctness of the tints exhibited by the precipitates considered in § 180, 3, *b*, *β* (58), it is advisable, in all cases where the least impurity is suspected, to adopt the following method for the detection of manganese, chromium, zinc, alumina, and silicic acid.

Add solution of soda to a portion of the original solution, first in small quantity, then in excess. 61

aa. No precipitate is formed: SILICIC ACID may be assumed to be present; proceed as directed § 180, 3, *b*, *β*, *aa* (60).

bb. A whitish precipitate is formed, which does not redissolve in an excess of the precipitant, and speedily turns blackish-brown upon exposure to the air: MANGANESE. The blowpipe is resorted to as a conclusive test (§ 106).

cc. A precipitate is formed which redissolves in an excess of the precipitant: SESQUIOXIDE OF CHROMIUM, ALUMINA, OXIDE OF ZINC.

aa. Add hydrosulphuric acid water to a portion of the

alkaline solution. The formation of a white precipitate indicates the presence of ZINC.

ββ. If the original or the alkaline solution is green, and if the precipitate produced by soda and redissolved by an excess of the precipitant, was of a bluish color, SESQUIOXIDE OF CHROMIUM is present. To remove all doubt, heat the alkaline solution to boiling, or try the reaction before the blowpipe (§ 101).

γγ. Add chloride of ammonium to the alkaline solution. The formation of a white precipitate indicates the presence of ALUMINA. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 100).

4. Add to a portion of the original solution chloride of ammonium and carbonate of ammonia, mixed with some caustic ammonia, and heat gently. **62**

a. NO PRECIPITATE IS FORMED: absence of baryta, strontia, and lime. Pass on to § 180, 5 (**64**).

b. A PRECIPITATE IS FORMED: presence of baryta, strontia, or lime. **63**

Add a considerable quantity of solution of sulphate of lime to a portion of the original solution.

α. *The solution does not become turbid, not even after the lapse of from five to ten minutes:* LIME. To remove all doubt, test with oxalate of ammonia (§ 96).

β. *The solution becomes turbid, but only after the lapse of some time:* STRONTIA. The alcohol flame will afford conclusive proof (§ 95).

γ. *A precipitate is immediately formed:* BARYTA. To remove all doubt, test with hydrofluosilicic acid (§ 94).

5. Mix that portion of the solution of 4 in which carbonate of ammonia has, after previous addition of chloride of ammonium, failed to produce a precipitate, with phosphate of soda, add some more ammonia, and rub the sides of the vessel with a glass rod. **64**

a. NO PRECIPITATE IS FORMED: absence of magnesia. Pass on to § 180, 6 (**65**).

b. A CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIA.

6. Evaporate a drop of the original solution on perfectly clean platinum foil as slowly as possible, and gently ignite the residue. **65**

a. THERE IS NO FIXED RESIDUE LEFT. Test for ammonia, by adding to the original solution hydrate of lime, and observing the odor and reaction of the escaping gas, and the fumes which it forms with acetio acid (§ 90).

b. THERE IS A FIXED RESIDUE LEFT: potassa or soda. Add bichloride of platinum to a portion of the original solution, having first concentrated it by evaporation if dilute, and shake the mixture. **66**

α. *No precipitate is formed, not even after the lapse of ten or fifteen minutes:* SODA. The blowpipe flame and alcohol flame are selected as conclusive tests, or the reaction with antimonate of potassa is resorted to for the purpose (§ 89).

β. *A yellow crystalline precipitate is formed:* POTASSA.

The reaction with tartaric acid, the blowpipe flame and alcohol flame are selected as conclusive tests (§ 88).

Simple Compounds.

A. Substances soluble in Water. Detection of the Acid.

I. *Detection of Inorganic Acids.*

§ 181.

Reflect in the first place *which* of the inorganic acids form soluble compounds with the detected base (compare Appendix IV.), and bear this in mind in your subsequent operations.

1. Arsenious acid and arsenic acid have already been considered in the preceding paragraph (detection of the base). These two acids are distinguished from each other by their respective behavior with nitrate of silver, or with potassa and sulphate of copper (see § 133). 67

2. The presence of carbonic acid, hydrosulphuric acid, and chromic acid, is also indicated already in the course of the process pursued for the detection of the bases. The two former betray their presence by effervescing upon the addition of hydrochloric acid; they may be distinguished from one another by their odor. Should additional proof be required, the presence of carbonic acid may be ascertained beyond a doubt by the reaction with lime-water (see § 149), and that of hydrosulphuric acid by the reaction with solution of acetate of lead (§ 156). The presence of chromic acid is invariably indicated by the yellow or red tint of the solution, as well as by the transition of the red or yellow color to green, accompanied by the separation of sulphur, upon the addition of hydrosulphuric acid water. To remove all doubt, try the reactions with solutions of acetate of lead and of nitrate of silver (§ 138, *b*). 68

3. Add some chloride of barium to a portion of the solution, then— if the fluid has remained clear, and the reaction is acid—ammonia to slightly alkaline reaction. 69

a. The fluid remains clear. Pass on to § 181, 4 (**71**). The absence of sulphuric acid, phosphoric acid, and silicic acid is certain, that of oxalic acid and boracic acid probable; as the baryta compounds of the two latter acids are kept in solution by ammoniacal salts, whilst borate of baryta does not separate from *dilute* solutions, even in the absence of ammoniacal salts.

b. A precipitate is formed. Add dilute hydrochloric acid in moderate excess. 70

α. The precipitate dissolves: absence of sulphuric acid. Pass on to 4 (**71**).

β. The precipitate remains undissolved, even on the addition of a large quantity of water: sulphuric acid.

4. Add solution of sulphate of lime to another portion of the solution (which, if it has an acid reaction, must first be neutralized, or made slightly alkaline, by means of ammonia). If no salt of ammonia is present, add some chloride of ammonium before adding the solution of sulphate of lime. 71

a. NO PRECIPITATE IS FORMED: absence of phosphoric acid, silicic acid, oxalic acid, and fluorine. Pass on to 5 (73).

b. A PRECIPITATE IS FORMED. Add acetic acid in excess. 72

α. The precipitate redissolves readily: PHOSPHORIC ACID or SILICIC ACID. The reaction with molybdic acid (§ 143) will afford conclusive proof of the presence of the former acid; to obtain positive certainty as to the presence of the latter, evaporate the solution, acidified with hydrochloric acid, to dryness, and treat the residue with hydrochloric acid.

β. The precipitate remains undissolved or dissolves with difficulty: OXALIC ACID or FLUORINE. Oxalate of lime is pulverulent, fluoride of calcium flocculent and gelatinous. The reaction with binoxide of manganese and sulphuric acid (§ 146) will afford conclusive proof of the presence of oxalic acid; the reaction on glass (etching) of the presence of fluorine (§ 147).

5. Acidify a fresh portion of the original solution with nitric acid, 73
and add solution of nitrate of silver.

a. THE FLUID REMAINS CLEAR. This is a proof of the absence of chlorine, bromine, iodine, ferrocyanogen, and ferricyanogen; the absence of cyanogen (in simple cyanides) is also probable. Of the soluble metallic cyanides, cyanide of mercury is not precipitated by nitrate of silver; if, therefore, in the analytical process for the detection of the bases, mercury has been found, cyanide of mercury may be present. For the manner of detecting the cyanogen in the latter, see § 155, 8. Pass on to 6 (76).

b. A PRECIPITATE IS FORMED.

α. The precipitate is orange: FERRICYANOGEN; the reaction 74
with sulphate of protoxide of iron is resorted to as a confirmatory test (§ 155, Appendix).

β. The precipitate is white or yellowish-white. Add ammonia in excess.

aa. The precipitate is not dissolved: IODINE or FERROCYANOGEN. In the former case the precipitate is pale yellow, in the latter white and gelatinous. The reaction with starch and hyponitric acid (§ 154) will afford conclusive proof of the presence of iodine, the reaction with sesquichloride of iron of the presence of ferrocyanogen (§ 155, Supplement).

ββ. The precipitate is dissolved: CHLORINE, BROMINE, 75
or CYANOGEN. If the original substance smells of hydrocyanic acid, and the silver precipitate dissolves with some difficulty in the ammonia, the precipitate may be assumed to consist of cyanide of silver, and, consequently, to indicate the presence of CYANOGEN. To remove all doubt on the point, add to the original solution sulphate of protoxide of iron, solution of soda, and hydrochloric acid (§ 155). If addition of chlorine water imparts a yellow tint to the original solution the precipitate may be held to consist of bromide of silver, and consequently indicates the presence of BROMINE; if the bromine is present only in very small proportion, ether must be used in conjunction with

chlorine water to make the reaction distinctly apparent (§ 153). In the proved absence of both bromine and cyanogen, the precipitate consists of chloride of silver, and consequently shows the presence of CHLORINE.

6. Add to a small portion of the aqueous solution hydrochloric 76
acid, drop by drop, until a distinct acid reaction is just imparted to the fluid, then dip in a slip of turmeric paper, take it out, and dry it. If the dipped portion looks brownish-red, BORACIC ACID is present. To settle all doubt on the point, add sulphuric acid and alcohol, and set fire to the latter (§ 145).

7. With regard to NITRIC ACID and CHLORIC ACID, these are 77
usually discovered already in the course of the preliminary examination (see § 174, 2, c [6]). The reaction with sulphate of protoxide of iron and sulphuric acid (§ 159) will afford conclusive evidence of the presence of the former, treatment of the solid salt with concentrated sulphuric acid, of the presence of the latter acid (§ 160).

Simple Compounds.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

II. *Detection of Organic Acids.*

§ 182.

1. Add ammonia to a portion of the aqueous solution of the 78
compound under examination to slight alkaline reaction, then chloride of calcium. If the solution was neutral, or only slightly acid, add chloride of ammonium before adding the chloride of calcium.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER SHAKING THE FLUID NOR AFTER THE LAPSE OF A FEW MINUTES: absence of oxalic acid and tartaric acid. Pass on to § 182, 2 (80).

b. A PRECIPITATE IS FORMED. Add lime-water in excess 79
to a fresh portion of the original solution, and then add solution of chloride of ammonium to the precipitate formed.

α. The precipitate redissolves: TARTARIC ACID. The reaction with acetate of potassa may be resorted to as a confirmatory test; but a still more positive proof will be afforded by the deportment which the precipitate produced by the chloride of calcium, and properly washed, exhibits with solution of soda or with ammonia and nitrate of silver (§ 162).

β. The precipitate does not redissolve: OXALIC ACID. To remove all doubt, try the reaction with concentrated sulphuric acid (§ 146).

2. Heat the fluid of 1, *a*, to boiling, keep at that temperature 80
for some time, and add some more ammonia to the boiling fluid.

a. IT REMAINS CLEAR: absence of citric acid. Pass on to § 182, 3 (81).

b. IT BECOMES TURBID, AND DEPOSITS A PRECIPITATE: CITRIC ACID. To remove all doubt as to the nature of the acid, add solution of acetate of lead in excess, wash the precipitate formed, and see whether it dissolves readily in ammonia (§ 163).

3. Mix the fluid of 2, *a*, with alcohol. 81

a. IT REMAINS CLEAR: absence of malic acid. Pass on to § 182, 4 (**82**).

b. A PRECIPITATE IS FORMED: MALIC ACID. To remove all doubt, it is *invariably* necessary to try the reaction with acetate of lead, to see whether the precipitate produced by that reagent dissolves with difficulty in ammonia, and to examine its deportment when the fluid in which it is suspended is heated to boiling (§ 164).

4. Neutralize a portion of the original solution *completely* (if not already absolutely neutral) with ammonia or with hydrochloric **82**
acid, and add solution of sesquichloride of iron.

a. A BULKY PRECIPITATE FORMS, OF A CINNAMON BROWN, OR DIRTY YELLOW COLOR. Wash the precipitate, heat it with ammonia, filter, concentrate the filtrate by evaporation, divide into two parts, and add to the one some hydrochloric acid, to the other alcohol and chloride of barium. The formation of a precipitate in the first portion indicates the presence of BENZOIC ACID, a precipitate in the second denotes the presence of SUCCINIC ACID. Compare § 167 and § 168.

b. THE LIQUID ACQUIRES A RATHER INTENSE DEEP RED TINT, **83**
AND, UPON PROTRACTED BOILING, A LIGHT REDDISH-BROWN PRECIPITATE SEPARATES: acetic acid or formic acid. Heat a portion of the solid salt under examination, or, if the substance is in the fluid state, of the residue left upon evaporating the fluid (which, if acid, you must neutralize first with soda), with sulphuric acid and alcohol (§ 170). The characteristic odor of acetic ether indicates the presence of ACETIC ACID.

If you do not detect acetic acid in the fluid, you may conclude that the substance under examination contains FORMIC ACID: to remove all doubt, try the reactions with nitrate of silver and chloride of mercury (§ 171).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

*Detection of the Base.**

§ 183.

Dilute a portion of the solution in hydrochloric acid, nitric acid, **84**
or nitrohydrochloric acid with water,† and proceed exactly as directed § 180, beginning at 1 (**46**), in cases where the substance is dissolved in nitric acid, and at 2 (**50**), if the solution already contains hydrochloric acid. Particular regard must be had in this to the following observations: we have seen § 180, 3, *b*, *β*, *cc* (**59**), that if, in cases where we

* Regard is also had here to certain salts of the alkaline earths, as this course of examination leads directly to their detection.

† If upon the addition of water the liquid becomes white and turbid or deposits a white precipitate, this indicates the presence of antimony or bismuth. Compare § 176, 4 (**29**). Heat with hydrochloric acid until the fluid has become clear again, and then pass on to § 180, 2 (**50**).

have A SUBSTANCE SOLUBLE IN WATER, we obtain, in the course of the examination, a white precipitate upon adding chloride of ammonium, ammonia, and sulphide of ammonium, this precipitate can consist only of sulphide of zinc, or alumina, or hydrate of silicic acid. But the case is different if the body is INSOLUBLE IN WATER, but dissolves in hydrochloric acid; for in that case a white precipitate produced by sulphide of ammonium, in presence of chloride of ammonium, may consist also of phosphates, borates, oxalates, silicates of the alkaline earths, or of fluorides of their metals, or all their bodies are insoluble in water, but dissolve in hydrochloric acid, and (being only very sparingly soluble also in solution of chloride of ammonium) accordingly separate again upon neutralization of that acid. If, therefore, a white precipitate is produced upon testing an acid solution, under the circumstances stated, and according to the directions of § 180, 3, *b*, *β*, *cc* (**59**) proceed as follows:—

1. If the results of the preliminary examination have given you reason **85**
to suspect the presence of SILICIC ACID (§ 174, 4, *b*, *a* [**20**]), evaporate a portion of the hydrochloric acid solution to dryness, moisten the residue with hydrochloric acid and add water. If silicic acid is present, it will remain undissolved. Determine the base in the solution as directed § 180, 3 (**56**), or 4 (**62**).

2. Add to a portion of the original hydrochloric acid solution some tartaric acid, and after this ammonia in excess.

a. NO PERMANENT PRECIPITATE IS FORMED: absence of the **86**
above enumerated salts of the alkaline earths. Mix another portion of the original solution with solution of soda in excess, and add to the one half of the clear fluid chloride of ammonium, to the other half hydrosulphuric acid. The formation of a precipitate in the former indicates the presence of ALUMINA; in the latter, the presence of ZINC. Whether the alumina was combined with PHOSPHORIC ACID, may be ascertained by testing a portion of the original hydrochloric acid solution with molybdate of ammonia (143).

b. A PERMANENT PRECIPITATE IS FORMED: presence of a salt of an alkaline earth.

α. If by ignition of the substance in a glass tube (in the **87**
course of the preliminary examination—see § 174, 2) carbonic oxide and carbonic acid have been evolved, the body turning slightly black in the process, you may assume the presence of an OXALATE. Heat a sample of the original substance to slight redness, dissolve the residue with hydrochloric acid, when ensuing effervescence will confirm the presence of oxalic acid; and ascertain the nature of the alkaline earth in the solution as directed § 180, 4 (**62**).

β. Add to a portion of the hydrochloric acid solution ammo- **88**
nia until a precipitate forms; then acetic acid until this is redissolved; lastly, acetate of soda and a drop of solution of sesquichloride of iron: the formation of a white flocculent precipitant indicates the presence of PHOSPHORIC ACID. Add now some more sesquichloride of iron until the fluid has acquired a distinct red color, boil, filter boiling, and test the filtrate, which is now free from phosphoric acid, for the alkaline earth with which the phosphoric acid was combined, as directed § 180, 4

(62), after having previously removed, by precipitation with ammonia, the iron which may have been dissolved.

γ. Test a portion of the original substance, or of the precipitate produced in the hydrochloric acid solution by ammonia, with sulphuric acid for FLUORINE (§ 147). After removal of the fluorine, ascertain the nature of the alkaline earth now in the residue, combined with sulphuric acid. 89

δ. BORACIC ACID is detected in the hydrochloric acid solution by means of turmeric paper (§ 145), and the base combined with it, by means of solution of sulphate of lime (baryta, strontia), sulphuric acid, and alcohol (lime), or a large proportion of chloride of ammonium, ammonia, and phosphate of soda (magnesia).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACID.

I. *Detection of Inorganic Acids.*

§ 184.

1. CHLORIC ACID cannot be present, since all chlorates without exception are soluble in water; NITRIC ACID, which may be present in form of a basic salt, must have been revealed already by ignition of the body in a glass tube (§ 174), and so must CYANOGEN (§ 174, 2, *e* [8]). For the analysis of the insoluble metallic CYANIDES insoluble in water see § 202. The results of the test with phosphate of soda and ammonia will have directed attention to the presence of SILICIC ACID (§ 174, 4, *b*, *a* [20]). Evaporation of the hydrochloric acid solution to dryness, and treatment of the residue with hydrochloric acid and water will set all doubt at rest on the point. 90

2. The course of examination laid down here for the detection of the bases leads likewise to that of ARSENIOUS and ARSENIC ACIDS, CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID. With regard to the latter acid, I repeat that its presence is indicated by the yellow or red color of the compound, the evolution of chlorine which ensues upon boiling with hydrochloric acid, and the subsequent presence of sesquioxide of chromium in the solution. Fusion of the compound under examination with carbonate of soda is, however, the most conclusive test for chromic acid (§ 138). 91

3. Boil a portion of the substance with nitric acid. 92

a. If nitric oxide gas is evolved, and sulphur separates, this is confirmative of the presence of a metallic sulphide.

b. If violet vapors escape, the compound is a metallic IODIDE.

c. If reddish-brown fumes of a chlorine-like smell are evolved, the compound is a metallic BROMIDE, in which case the fumes will color starch yellow (§ 153).

4. Dilute a portion of the solution obtained by boiling with nitric acid (3 [92])—or of the filtrate of this solution, should the nitric acid have left an undissolved residue—with water, and add solution of nitrate of silver to the fluid. The formation of a white precipitate 93

which, after washing, is soluble in ammonia, and fuses without decomposition when heated, indicates the presence of CHLORINE.

5. Boil a portion of the substance with hydrochloric acid, filter, if 94
necessary, dilute with water, and add chloride of barium. The formation of a white precipitate, which does not redissolve even upon addition of a large quantity of water, indicates the presence of SULPHURIC ACID.

6. Test for BORACIC ACID as directed § 181, 6 (76).

7. If none of the acids enumerated from 1 to 6 are present, there 95
is reason to suspect the presence of PHOSPHORIC ACID, OXALIC ACID, or FLUORINE, or the total absence of acids. To the presence of oxalic acid your attention will have been called already in the course of the preliminary examination, § 174, 2, *e* (8). If the acids named had been combined with an alkaline earth, or, as regards phosphoric acid, with alumina, they would already have been detected in the course of the examination for these bases (§ 183); they need therefore here be tested for, only in case the examination has revealed the presence of some other base. To that end, precipitate the base, according to circumstances, either with hydrosulphuric acid or with sulphide of ammonium, and filter. If you have precipitated with sulphide of ammonium, add to the filtrate hydrochloric acid to acid reaction, expel in either case the hydrosulphuric acid by boiling, and filter if necessary. Test a portion of this solution for phosphoric acid, oxalic acid, and fluorine, as directed § 181, 4 (71).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN ACIDS.

DETECTION OF THE ACID.

II. *Detection of Organic Acids.*

§ 185.

1. FORMIC ACID cannot be present, as all the formates are soluble 96
in water.

2. ACETIC ACID has been revealed already in the course of the preliminary examination, by the disengagement of acetone. The reaction with sulphuric acid and alcohol (§ 170) will afford conclusive proof.

3. Boil a portion of the substance for some time with solution of 97
carbonate of soda in excess, and filter hot. You have now the organic acid in solution in combination with soda. Acidulate the solution slightly with hydrochloric acid, expel the carbonic acid by heat, and test as directed § 182.

Simple Compounds.

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, AND NITROHYDROCHLORIC ACID.

DETECTION OF THE BASE AND THE ACID.

§ 186.

Under this head we have to consider here, SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, FLUORIDE OF CALCIUM, SILICA, SULPHATE OF LEAD, compounds of LEAD with CHLORINE and BROMINE, compounds of SILVER with CHLORINE, BROMINE, IODINE, and CYANOGEN, and lastly, SULPHUR and CHARCOAL, as the only bodies belonging to this class which are more frequently met with. For the simple silicates I refer to § 203, for the ferro- and ferricyanides, to § 202. The preliminary examination will have informed you whether you need pay any regard to the possible presence of their compounds. 98

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are so difficultly soluble that complete solution of them is seldom effected, they are included here also among the class of insoluble substances, to insure their detection, should they have been overlooked in the course of the examination of the aqueous or acid solution of the body to be analyzed.

1. Free SULPHUR must have been detected already in the course of the preliminary examination.

2. CHARCOAL is black; it is insoluble in aqua regia; put on platinum foil, with the blowpipe flame playing upon the under side of the foil, it is always consumed; by deflagration with nitrate of potassa it yields carbonate of potassa.

3. Pour sulphide of ammonium over a very small quantity of the substance under examination. 99

a. It TURNS BLACK; this indicates the presence of lead or a salt of silver.

α. *The body fused in the glass tube without decomposition* (§ 174, 2 [3]): chloride of lead, bromide of lead, chloride of silver, bromide of silver, iodide of silver. Fuse 1 part of the compound with 4 parts of carbonate of soda and potassa in a small porcelain crucible, let cool, boil the residue with water, and test the filtrate for CHLORINE, BROMINE, and IODINE, as directed, § 181, 5 (73). Dissolve the residue, which consists either of metallic SILVER or OXIDE OF LEAD, in nitric acid, and test the solution as directed, § 180, 1 (46).

β. *The body evolved cyanogen, and left metallic silver behind:* CYANIDE OF SILVER.

γ. *The body remained unaltered:* SULPHATE OF LEAD. Boil a sample of it with solution of carbonate of soda, filter, acidulate the filtrate with hydrochloric acid, and test with chloride of barium for SULPHURIC ACID; dissolve the washed residue in nitric acid, and test the solution with hydrosulphuric acid and with sulphuric acid for LEAD.

b. IT REMAINS WHITE: absence of an oxide of a heavy metal. 100

a. The body fused before the blowpipe; this indicates the presence of FLUORIDE OF CALCIUM. Reduce a portion of the substance to a fine powder, decompose this in a platinum crucible with sulphuric acid, and try the reaction on glass (§ 147), to prove the presence of FLUORINE; boil the residue with hydrochloric acid, filter, neutralize the filtrate with ammonia, and test for LIME with oxalate of ammonia.

β. The body did not fuse before the blowpipe. Mix a small portion of the very finely pulverized substance with 4 times the quantity of pure carbonate of soda and potassa, and fuse the mixture in a platinum crucible, or else on platinum foil. Boil the fused mass with water, filter, should a residue be left, and wash the latter. Acidulate a portion of the filtrate with hydrochloric acid, and then test with chloride of barium for SULPHURIC ACID; and in case you do not find that acid, test another portion of the filtrate for SILICIC ACID, by evaporating the fluid acidified with hydrochloric acid.

If the SILICIC ACID was present in the pure state, the mass resulting from the fusion of the substance with carbonate of soda and potassa must have dissolved in water to a clear fluid; but if silicates also happened to be present, the bases of them are left behind undissolved, and may be further examined.

If, on the other hand, sulphuric acid has been found, the alkaline earth which was combined with it is found on the filter as a carbonate. Wash this, then dissolve it in dilute hydrochloric acid, and test the solution for BARYTA, STRONTIA, and LIME, as directed § 180, 4 (62).

*Complex Compounds.**

A. SUBSTANCES SOLUBLE IN WATER, AND ALSO SUCH AS ARE INSOLUBLE IN WATER, BUT DISSOLVE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

Detection of the Bases.†

§ 187.‡

(Treatment with Hydrochloric Acid: Detection of Silver, Suboxide of Mercury [Lead].)

The systematic course for the detection of the bases is essentially the same for bodies soluble in water, as for those which are soluble only in acids. Where, in consequence of the different nature of the original solution, deviations are rendered necessary, the fact will be distinctly stated. 101

* I use this term here, and hereafter in the present work, to designate compounds in which all the more frequently occurring bases, acids, metals, and metalloids are supposed to be present.

† Consult the explanations in the Third Section. Regard is here had also to the presence of the acids of arsenic, and of those salts of the alkaline earths which dissolve in hydrochloric acid, and separate again from that solution unaltered, upon neutralization of the acid by ammonia.

‡ Consult the remarks in the Third Section.

I. Solution in Water.

Mix the portion intended for the detection of the bases with some hydrochloric acid.

1. The solution had an acid or neutral reaction previously to the addition of the hydrochloric acid. 102

a. No precipitate is formed; this indicates the absence of silver and suboxide of mercury. Pass on to § 188.

b. A precipitate is formed. Add more hydrochloric acid drop by drop until the precipitate ceases to increase; then add about six or eight drops more of hydrochloric acid, shake the mixture, and filter.

The precipitate produced by hydrochloric acid may consist of chloride of silver, subchloride of mercury, chloride of lead, a basic salt of antimony, possibly also of benzoic acid. The basic salt of antimony, however, redissolves in the excess of hydrochloric acid; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of chloride of silver, subchloride of mercury, or chloride of lead—(possibly also of benzoic acid, which, however, is altogether disregarded *here*).

Wash the precipitate collected upon the filter twice with cold water, add the washings to the filtrate, and examine the solution as directed § 188, even though the addition of the washings to the acid filtrate should produce turbidity in the fluid (which indicates the presence of compounds of antimony or bismuth).

Treat the washed precipitate on the filter as follows: 103

α. Pour hot water over it upon the filter, and test the fluid running off with sulphuric acid for lead. The non-formation of a precipitate upon the addition of the sulphuric acid simply proves that the precipitate produced by hydrochloric acid contains no lead, and does not by any means establish the total absence of this metal, as hydrochloric acid fails to precipitate lead from dilute solutions.

β. Pour over the now thrice-washed precipitate upon the filter solution of ammonia. If this changes its color to black or gray, it is a proof of the presence of suboxide of mercury.

γ. Add to the ammoniacal fluid running off in *β* nitric acid to strongly acid reaction. The formation of a white, curdy precipitate indicates the presence of silver.* (If the precipitate did contain lead, the ammoniacal solution generally appears turbid, owing to the separation of a basic salt of lead. This, however, does not interfere with the testing for silver, since the basic salt of lead redissolves upon the addition of nitric acid.)

2. The original aqueous solution had an alkaline reaction. 104

a. The addition of hydrochloric acid to strongly acid

* If the quantity of silver is only very small, the presence is indicated by opalescence of the fluid.

REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON FURTHER ADDITION OF HYDROCHLORIC ACID: pass on to § 188.

b. THE ADDITION OF HYDROCHLORIC ACID TO THE ORIGINAL SOLUTION PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, EVEN UPON BOILING.

α. The formation of the precipitate is attended neither with evolution of hydrosulphuric acid nor of hydrocyanic acid. 105
Filter, and treat the filtrate as directed § 188.

aa. THE PRECIPITATE IS WHITE. It may, in that case, consist of a salt of lead or silver, insoluble in water and hydrochloric acid (CHLORIDE OF LEAD, SULPHATE OF LEAD, CHLORIDE OF SILVER, &c.). Test for the bases and acids of these compounds as directed § 201, bearing in mind that the chloride of lead or chloride of silver which may be present may possibly have been formed in the process.

bb. THE PRECIPITATE IS YELLOW OR ORANGE. In that case it may consist of SULPHIDE OF ARSENIC (and if the fluid from which it has separated was not boiled for a long time, or only with very dilute hydrochloric acid, also of sulphide of antimony or bisulphide of tin), which substances were originally dissolved in solution of ammonia, borax, phosphate of soda, or some other alkaline fluid, with the exception of solutions of alkaline sulphides and cyanides. Examine the precipitate as directed § 190.

*β. The formation of the precipitate is attended with evolution of hydrosulphuric acid gas, but not of hydrocyanic acid.** 106

aa. THE PRECIPITATE IS OF A PURE WHITE COLOR, AND CONSISTS OF SEPARATED SULPHUR. In that case a SULPHURETTED ALKALINE SULPHIDE is present. Boil, filter, and pass on to § 192, bearing in mind that of the substances considered in that paragraph the heavy metals cannot be present if the original solution was colorless.

bb. THE PRECIPITATE IS COLORED. In that case you may conclude that a METALLIC SULPHUR SALT is present, *i. e.*, a combination of an alkaline sulphur base with a metallic sulphur acid. The precipitate may accordingly consist of TERSULPHIDE OF GOLD, BISULPHIDE OF PLATINUM, BISULPHIDE OF TIN, TERSULPHIDE OF ARSENIC, or TERSULPHIDE OF ANTIMONY. It might, however, consist also of SULPHIDE OF MERCURY or of SULPHIDE OF COPPER, or contain these substances, as the former is readily soluble in sulphide of potassium, and the latter slightly soluble in sulphide of ammonium. Filter, and treat the filtrate as in *aa*, the preciptate as directed § 189.

γ. The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of hydrosulphuric acid. This indicates the pre- 107

* Should the odor of the evolved gas leave any doubt regarding the presence or absence of hydrocyanic acid, add some chromate of potassa to a portion of the fluid, previously to the addition of the hydrochloric acid.

sence of an ALKALINE CYANIDE, and, if the evolution of the hydrocyanic acid is attended with that of hydrosulphuric acid, also of an alkaline SULPHIDE. In that case the precipitate may, besides the compounds enumerated in α (105) and β (106), contain many other substances (*e. g.*, sulphide of nickel, cyanide of nickel, cyanide of silver, &c.). Boil, with further addition of hydrochloric acid, or of nitric acid, until the whole of the hydrocyanic acid is expelled, and treat the solution, or, if an undissolved residue has been left, the filtrate, as directed § 188; and the residue (if any) according to § 201.

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS. **108**

α. *The escaping gas smells of hydrosulphuric acid;* this indicates the presence of a SIMPLE ALKALINE SULPHIDE. Proceed as in *b*, β, *aa* (106).

β. *The escaping gas is inodorous;* in that case it is CARBONIC ACID which was combined with an alkali. Pass on to § 188.

γ. *The escaping gas smells of hydrocyanic acid* (no matter whether hydrosulphuric acid or carbonic acid is evolved at the same time or not). This indicates the presence of an ALKALINE CYANIDE. Boil until the whole of the hydrocyanic acid is expelled, and then pass on to § 188.

II. SOLUTION IN HYDROCHLORIC ACID OR IN NITROHYDROCHLORIC ACID.

Proceed as directed § 188.

III. SOLUTION IN NITRIC ACID.

Dilute a small sample of it with water; should this produce turbidity or a precipitate (indicative of the presence of bismuth) add nitric acid until the fluid is clear again, then hydrochloric acid. **109**

1. NO PRECIPITATE IS FORMED. Absence of silver and suboxide of mercury. Treat the principal solution as directed § 188.

2. A PRECIPITATE IS FORMED. Treat a larger portion of the nitric acid solution the same way as the sample, filter, and examine the precipitate as directed § 187, I. 1, *b* (103), the filtrate as directed § 188.

§ 188.*

(Treatment with Hydrosulphuric Acid, Precipitation of the Metallic Oxides of Group V. *2nd Section, and of Group* VI.)

ADD TO A *small* PORTION OF THE CLEAR ACID SOLUTION HYDROSULPHURIC ACID WATER, UNTIL THE ODOR OF HYDROSULPHURIC ACID IS DISTINCTLY PERCEPTIBLE AFTER SHAKING THE MIXTURE, AND WARM GENTLY.

1. NO PRECIPITATE IS FORMED, even after the lapse of some **110**

* Consult the remarks in the Third Section.

time. Pass on to § 192, for lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic,* are not present;† the absence of sesquioxide of iron and of chromic acid is also indicated by this negative reaction.

2. A PRECIPITATE IS FORMED.

111 *a. The precipitate is of a pure white color*, light and finely pulverulent, and does not redissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of SESQUIOXIDE OF IRON.‡ None of the other metals enumerated in § 188, 1 (**110**), can be present. Treat the principal solution as directed § 192.

b. The precipitate is colored.

112 Add to the larger proportion of the acid or acidified solution, best in a small flask, hydrosulphuric acid water in excess, *i. e.*, until the fluid smells distinctly of it, and the precipitate ceases to increase upon continued addition of the reagent; apply a gentle heat, shake vigorously for some time, filter, keep the filtrate (which contains the oxides present of Groups I.—IV.) for further examination, according to the instructions of § 192, and thoroughly wash the precipitate which contains the sulphides of the metals present of Groups V. and VI.

In many cases, and more particularly when there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit hydrosulphuric acid gas through the solution DILUTED WITH WATER, instead of adding hydrosulphuric acid water.

113 If the precipitate is yellow, it consists principally of tersulphide of arsenic, bisulphide of tin, or sulphide of cadmium; if orange-colored, this indicates tersulphide of antimony; if brown or black, one at least of the following oxides is present: oxide of lead, teroxide of bismuth, oxide of copper, oxide of mercury, teroxide of gold, binoxide of platinum, protoxide of tin. However, as a yellow precipitate may contain small admixtures of an orange-colored, a brown, or even a black precipitate, and yet its color not be very perceptibly altered thereby, it will always prove the safest way to assume the presence of all the metals named in § 188, 1 (**110**), in any precipitate produced by hydrosulphuric acid, and to proceed accordingly as the next paragraph (§ 189) directs.

* Should the preliminary examination have led you to suspect the presence of arsenic acid, you must endeavor to obtain the most conclusive evidence of the absence of this acid; this may be done by allowing the fluid to stand for some time, or by heating it with sulphurous acid previous to the addition of the hydrosulphuric acid. (Compare § 132.)

† In solutions containing much free acid, the precipitates are frequently formed only after dilution with water.

‡ Sulphur will precipitate also if sulphurous acid, iodic acid, or bromic acid are present (which substances are not included in our analytical course), and also if chromic acid, chloric acid, or free chlorine are present. In presence of chromic acid, the separation of the sulphur is attended with reduction of the acid to sesquioxide of chromium, in consequence of which the reddish-yellow color of the solution changes to green. (Compare § 138.) The white sulphur suspended in the green solution looks at first like a green precipitate, which frequently tends to mislead beginners.

§ 189.

(*Treatment of the Precipitate produced by Hydrosulphuric Acid with Sulphide of Ammonium; Separation of the 2nd Section of Group V. from Group VI.*)

INTRODUCE A SMALL PORTION OF THE PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID IN THE ACIDIFIED SOLUTION INTO A TEST-TUBE,* ADD A LITTLE WATER, AND THREE OR FOUR DROPS OF YELLOWISH SULPHIDE OF AMMONIUM, AND EXPOSE THE MIXTURE FOR A SHORT TIME TO A GENTLE HEAT. † 114

1. THE PRECIPITATE DISSOLVES COMPLETELY IN SULPHIDE OF AMMONIUM (or SULPHIDE OF SODIUM, as the case may be): absence of the metals of Group V.—cadmium, lead, bismuth, copper, mercury. Treat the remainder of the precipitate (of which you have digested a portion with sulphide of ammonium) as directed § 190.—If the precipitate produced by hydrosulphuric acid was so trifling that you have used the whole of it in treating with sulphide of ammonium, precipitate the solution obtained in that process by addition of hydrochloric acid, filter, wash the precipitate, and treat the latter as directed § 190. 115

2. THE PRECIPITATE IS NOT REDISSOLVED, OR AT LEAST NOT COMPLETELY: presence of the metals of Group V. 116

Dilute with 4 or 5 parts of water, filter, and mix the filtrate with hydrochloric acid in slight excess.

a. The fluid simply turns milky, owing to the separation of sulphur. Absence of the metals of Group VI.—gold, platinum, tin, antimony, and arsenic.‡ Treat the rest of the precipitate of which you have digested a portion with sulphide of ammonium, according to the directions of § 191.

b. A colored precipitate is formed: presence of metals of Group VI. by the side of those of Group V. Treat the entire precipitate produced by hydrosulphuric acid the same as you have treated a portion of it, *i.e.*, digest it with yellow 117

* If there is a somewhat large precipitate, this may be readily effected by means of a small spatula of platinum or horn; but if you have only a very trifling precipitate, make a hole in the bottom of the filter, insert the perforated point into the mouth of the test-tube, rinse the precipitate into the latter by means of the washing-bottle, wait until the precipitate has subsided, and then decant the water.

† If the solution contains copper, which is generally revealed by the color of the fluid, and may be ascertained positively by testing with a clean iron rod (see § 119, 10), use solution of sulphide of sodium instead of sulphide of ammonium (in which sulphide of copper is not absolutely insoluble, see § 119, 5), and boil the mixture. But if the fluid, besides copper, also contains oxide of mercury (the presence of which is generally sufficiently indicated by the several changes of color exhibited by the precipitate forming upon the addition of the hydrosulphuric acid [§ 118, 3], and which, in doubtful cases, may be detected with positive certainty by testing a portion of the original solution acidified with hydrochloric acid, with protochloride of tin), sulphide of ammonium must be used, although the separation of the sulphides of the antimony group from the sulphide of copper is not fully effected in such cases; since, were sulphide of sodium used, the sulphide of mercury would dissolve in this reagent, and this would impede the ulterior examination of the sulphides of the antimony group.

‡ That this inference becomes uncertain if the precipitate produced by hydrosulphuric acid, instead of being digested with a small quantity of sulphide of ammonium, has been treated with a larger quantity of that reagent, is self-evident; for the large quantity of sulphur which separates in that case will, of course, completely conceal any slight traces of sulphide of arsenic or bisulphide of tin which may have been thrown down.

sulphide of ammonium, or, as the case may be, sulphide of sodium, let it subside, pour the supernatant liquid on a filter, digest the residue in the tube once more with yellow sulphide of ammonium (or sulphide of sodium), and filter. Wash the residue* (containing the sulphides of Group V.), and treat it afterwards as directed § 191. Dilute the filtrate —which contains the metals of Group VI. in the form of sulphur salts—with water, add hydrochloric acid to slightly acid reaction, heat gently, filter the precipitate formed—which contains the sulphides of the metals of Group VI. mixed with sulphur—wash thoroughly, and proceed as directed next paragraph (§ 190).

§ 190.

(*Detection of the Metals of Group* VI.: *Arsenic, Antimony, Tin, Gold, Platinum.*)

If the precipitate consisting of the sulphides of Group VI. has a PURE YELLOW COLOR, this indicates principally arsenic and tin; if it is distinctly ORANGE-YELLOW, antimony is present; if it is BROWN or BLACK, this denotes the presence of platinum or gold. 118

Beyond these general indications, the color of the precipitate affords no safe guidance. It is therefore always advisable to test yellow precipitate also for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely hid by a large quantity of bisulphide of tin or tersulphide of arsenic. Proceed accordingly as follows:

Heat a little of the precipitate on the lid of a porcelain crucible, or on a fragment of porcelain or glass.†

1. *Complete volatization ensues:* probable presence of ARSENIC, absence of the other metals of Group VI. Reduction of a portion of the precipitate with cyanide of potassium and carbonate of soda (§ 131, 12) will afford positive proof of the presence or absence of arsenic. Whether that metal was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the method described § 133. 119

2. *A fixed residue is left.* In that case all the metals of Group VI. must be sought for. Dry the remainder of the precipitate thoroughly upon the filter, triturate it together with about 1 part of anhydrous carbonate of soda and 1 part of nitrate of soda, and transfer the mixture in small portions at a time to a little porcelain crucible, in which you have previously 120

* If the residue suspended in the fluid containing sulphide of ammonium, and insoluble therein, subsides readily, it is not transferred to the filter, but washed in the tube by decantation. But if its subsidence proceeds slowly and with difficulty, it is transferred to the filter, and washed there; a hole is then made in the bottom of the filter, and the residue rinsed into a small porcelain basin by means of a washing-bottle; the application of a gentle heat will now materially aid the subsidence of the residue, and the supernatant water may then be decanted.

† That this preliminary examination may be omitted if the precipitate is not yellow, and that it can give a decisive result only if the sulphur precipitate submitted to the test has been thoroughly washed, is self-evident.

heated 2 parts of nitrate of soda to fusion.* As soon as complete oxidation is effected, pour the mass out on a piece of porcelain.

After cooling, soak the fused mass (the portion still sticking to the inside of the crucible as well as the portion poured out on the porcelain) in cold water, filter the insoluble residue—which will remain if the mass contained antimony, tin, gold, or platinum—and well wash with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the solution of the antimonate of soda. The washings are not added to the filtrate.) The filtrate and the residue are now examined as follows:

a. EXAMINATION OF THE FILTRATE FOR ARSENIC (which must be present in it in the form of arsenate of soda). 121

Divide the filtrate into two portions, add highly dilute nitric acid cautiously to the one portion to slightly acid reaction, and apply heat.† Add to the acidified solution some nitrate of silver (not too little), filter (in case some chloride of silver‡ or nitrite of silver should have separated), pour upon the filtrate, along the side of the tube held slanting, a layer of dilute solution of ammonia,—5 parts of water to 1 part of solution of ammonia—and let the mixture stand for some time without shaking. The formation of a reddish-brown precipitate, which appears hovering cloud-like between the two layers (and may be seen far more readily and distinctly by reflected than by transmitted light), denotes the presence of ARSENIC.

If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly saturated with ammonia, the fluid being stirred during this process, the precipitate of arsenate of silver which forms imparts a brownish-red tint to the entire fluid.

To gain more positive information respecting the presence of 122
arsenic, precipitate the second portion of the filtrate with solution of neutral acetate of lead, filter the precipitate (which consists of sulphate, carbonate, and—if arsenic is really present—arsenate of lead), dry between blotting paper, and then expose on charcoal to the inner flame of the blowpipe. If arsenic is present, a globule of metallic lead containing arsenic will be produced, which will long continue to exhale the odor of

* Should the amount of the precipitate be so minute that this operation cannot be conveniently performed, cut the filter, with the dried precipitate adhering to it, into small pieces, triturate these together with some carbonate of soda and nitrate of soda, and project both the powder and the paper into the fusing nitrate of soda. It is *preferable*, however, in such cases, to procure at once, if practicable, a sufficiently large amount of the precipitate, as otherwise there will be but little hope of effecting the positive detection of all the metals of Group VI. Supposing all the metallic sulphides of the sixth group to have been present, the fused mass would consist of antimonate and arsenate of soda, binoxide of tin, metallic gold and platinum, sulphate, carbonate, nitrate, and some nitrite of soda. Compare also § 133, 1.

† In some cases where a somewhat larger proportion of carbonate of soda had been used, or a very strong heat applied, a trifling precipitate (hydrated binoxide of tin) may separate upon the acidification of the filtrate with nitric acid. This may be filtered off, and then treated in the same manner as the undissolved residue.

‡ Chloride of silver will separate if the reagents were not perfectly pure, and the precipitate has not been thoroughly washed.

garlic whenever the inner flame of the blowpipe is made to act upon it. For further confirmation of the presence of arsenic this substance may be exhibited in the metallic state. (Compare § 131 and § 132.) Whether the arsenic was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the method described, § 133, at the end.

b. EXAMINATION OF THE RESIDUE FOR ANTIMONY, TIN, GOLD, PLATINUM. (As the antimony, if present in the residue, must exist as white, pulverulent antimonate of soda, the tin as white, flocculent binoxide, the gold and platinum in the metallic state, the appearance of the residue is in itself indicative of its nature.) Dry the residue on the filter. *If there is much of it*, separate it from the filter, and fuse it together with about 4 parts of cyanide of potassium, either in a small porcelain crucible or in a somewhat wide glass tube sealed at one end. *If the quantity is small*, insert the filter together with the precipitate in a platinum wire twisted into a spiral coil, and incinerate in the outer mantle of a small spirit-lamp or gas-flame; transfer the residue together with the filter-ash to a narrow glass tube sealed at one end, and fuse it in this together with 4 parts of cyanide of potassium; insert the ignited part of the tube, whilst still red-hot, into a test-tube filled with cold water, which will cause the part containing the fused mass to crack off in splinters. In either case remove the soluble salts completely by repeated warming with water and decantation, pour hydrochloric acid over the metallic residue, heat to boiling, and test the solution, which—in case of the presence of TIN—must contain protochloride of tin, with chloride of mercury (§ 128, 8). Boil the residue once more with hydrochloric acid, decant the fluid, then dissolve the residue still remaining in hydrochloric acid with addition of the least possible amount of nitric acid to effect solution, mix this with solution of hydrosulphuric acid, and heat to incipient boiling. 123

If a precipitate of a distinct orange color forms, ANTIMONY is present. In presence of much tin, the color is usually more or less concealed by an admixture of bisulphide of tin (for it is not easy to effect a complete separation of the two metals by boiling with hydrochloric acid); the precipitate may also contain bisulphide of platinum and metallic gold (resulting from the reduction by heat of precipitated tersulphide of gold). 124

Let the precipitate, therefore, subside, wash it several times by decantation, and finally heat it with hydrochloric acid, to dissolve the sulphide of antimony present. If the precipitate did contain gold or bisulphide of platinum, a black pulverulent residue will remain. Test now in the first place the hydrochloric acid solution for ANTIMONY, by means of zinc and platinum (§ 130, 8), then dissolve the residue, if any, in some nitrohydrochloric acid, and test a portion of the solution for GOLD, with protochloride of tin, another portion for the same metal with sulphate of protoxide of iron (§ 125). Evaporate the remainder of the solution with addition of some chloride of potassium, and add to the residue a mixture of equal parts of alcohol and water. The formation of a yellow precipitate indicates the presence of PLATINUM.

§ 191.

(Detection of the Metallic Oxides of Group V. 2nd Section :—Oxide of Lead. Teroxide of Bismuth. Oxide of Copper. Oxide of Cadmium. Oxide of Mercury.)

WASH THE PRECIPITATE WHICH HAS NOT BEEN DISSOLVED BY SUL- 125
PHIDE OF AMMONIUM, AND BOIL WITH NITRIC ACID. This operation is performed best in a small porcelain dish; the boiling mass must be constantly stirred with a glass rod during the process. A great excess of acid must be avoided.

1. THE PRECIPITATE DISSOLVES, AND THERE REMAINS FLOATING IN 126
THE FLUID ONLY THE SEPARATED, LIGHT, FLOCCULENT, YELLOW SULPHUR; this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH may be present.

Filter the fluid from the separated sulphur, and treat the filtrate as follows (should there be too much nitric acid present, the greater part of this must first be driven off by evaporation): add to a portion of the filtrate dilute sulphuric acid in moderate quantity, heat gently, and let the fluid stand some time.

a. NO PRECIPITATE FORMS; absence of lead. Mix the re- 127
mainder of the filtrate with ammonia in excess, and gently heat.

α. No precipitate is formed; absence of BISMUTH. If the 128
liquid is blue, COPPER is present; very minute traces of copper, however, might be overlooked, if the color of the ammoniated fluid alone were consulted. To be quite safe, and also to test for cadmium, evaporate the ammoniated solution nearly to dryness, add a little acetic acid, and, if necessary, some water, and

aa. Test a small portion of the fluid for copper with 129
ferrocyanide of potassium. The formation of a reddish-brown precipitate, or a light brownish-red turbidity, indicates the presence of COPPER (in the latter case only to a very trifling amount).

bb. Mix the remainder of the fluid with solution of 130
hydrosulphuric acid in excess. The formation of a yellow precipitate denotes CADMIUM. If, on account of the presence of copper, the sulphide of cadmium cannot be distinctly recognised, allow the precipitate produced by the hydrosulphuric acid to subside, decant the supernatant fluid, and add to the precipitate solution of cyanide of potassium until the sulphide of copper is dissolved. If a yellow residue is left undissolved, CADMIUM is present; in the contrary case, not.

β. A precipitate is formed. BISMUTH is present. Filter 131
the fluid, and test the filtrate for copper and cadmium, as directed in *α* (128). To test the washed precipitate more fully for bismuth, slightly dry the filter containing it between blotting-paper, remove the still moist precipitate with a platinum spatula, dissolve in a watch-glass in the least possible quantity of hydrochloric acid, and then add a

sufficient quantity of water. The appearance of a milky bidity confirms the presence of bismuth.

132 *b*. A PRECIPITATE IS FORMED. Presence of LEAD. Treat the entire fluid the same as you have treated the sample, filter off the precipitate of sulphate of lead, and test the filtrate for bismuth, copper, and cadmium, as directed in *a* (127).* Test the precipitate, after washing, by pouring solution of hydrosulphuric acid over it.

133 2. THE PRECIPITATE OF THE METALLIC SULPHIDES DOES NOT COMPLETELY DISSOLVE IN THE BOILING NITRIC ACID, BUT LEAVES A RESIDUE, BESIDES THE LIGHT FLAKES OF SULPHUR THAT FLOAT IN THE FLUID. Probable presence of OXIDE OF MERCURY (which may be pronounced almost certain, if the precipitate is heavy and black). Allow the precipitate to subside, filter off the fluid, which must still be tested for CADMIUM, COPPER, LEAD, and BISMUTH; mix a small portion of the filtrate with a large amount of solution of hydrosulphuric acid, and should a precipitate form or a coloration become visible, treat the remainder according to the directions of § 191, 1 (126).

Wash the residue (which, besides sulphide of mercury, may also contain sulphate of lead, formed by the action of nitric acid upon sulphide of lead, and also binoxide of tin, as the complete separation of bisulphide of tin from many of the sulphides of the metals of Group V. is rather difficult), and examine one half of it for mercury,† by dissolving it in some hydrochloric acid, with addition of a very small proportion of nitric acid, and testing the solution with copper, or protochloride of tin (§ 118); fuse the other half with cyanide of potassium and carbonate of soda. If you obtain metallic grains, wash, heat with nitric acid, and test the solution obtained with sulphuric acid for lead, the residue, which may be left, for tin, according to the directions of § 190, 2, *b* (123).

§ 192.

(*Precipitation with Sulphide of Ammonium, Separation and Detection of the Oxides of Groups* III. *and* IV. : *Alumina, Sesquioxide of Chromium;* —*Oxide of Zinc, Protoxide of Manganese, Protoxide of Nickel, Protoxide of Cobalt, Proto- and Sesquioxide of Iron; and also of those Salts of the Alkaline Earths which are precipitated by Ammonia from their Solution in Hydrochloric Acid; Phosphates, Borates, Oxalates, Silicates, and Fluorides.*)

134 PUT A *small portion* OF THE FLUID IN WHICH SOLUTION OF HYDROSULPHURIC ACID HAS FAILED TO PRODUCE A PRECIPITATE (§ 188, 1, [110]), OR OF THE FLUID WHICH HAS BEEN FILTERED FROM THE PRECI-

* For another method of distinguishing cadmium, copper, lead, and bismuth from each other, I refer to the Third Section (additions and remarks to § 191) page 274.

† If you have an aqueous solution, or a solution in very dilute hydrochloric acid, the oxide of mercury formed was present in the original substance in that form; but if the solution has been prepared by boiling with concentrated hydrochloric acid, or by heating with nitric acid, the mercury may most likely have been originally present in the form of suboxide, and may have been converted into oxide in the process.

PITATE FORMED, in a test-tube, observe whether it is colored or not,* boil to expel the hydrosulphuric acid which may be present, add a few drops of nitric acid, boil, and observe again the color of the fluid; then cautiously add ammonia to alkaline reaction, observe whether this produces a precipitate, and then add some sulphide of ammonium, no matter whether ammonia has produced a precipitate or not.

a. NEITHER AMMONIA NOR SULPHIDE OF AMMONIUM PRODUCES A PRECIPITATE. Pass on to § 193, for iron, nickel, cobalt, zinc, manganese, sesquioxide of chromium, alumina, are not present, nor are phosphates, borates,† silicates, and oxalates of the alkaline earths; nor fluorides of the metals of the alkaline earths. **135**

b. SULPHIDE OF AMMONIUM PRODUCES A PRECIPITATE, AMMONIA HAVING FAILED TO DO SO; absence of phosphates, borates,† silicates, and oxalates of the alkaline earths; of the fluorides of the metals of the alkaline earths; and also, if no organic matters are present, of iron, sesquioxide of chromium, and alumina. Pass on to § 192, 1 (**138**). **136**

c. AMMONIA PRODUCES A PRECIPITATE before the addition of sulphide of ammonium. The course of proceeding to be pursued now depends upon whether, (α) the original solution is simply aqueous, and has a neutral reaction, or (β) the original solution is acid. In the former case, pass on to § 192, 1 (**138**), for phosphates, borates, oxalates, and silicates of the alkaline earths cannot be present; nor can fluorides of the metals of the alkaline earths. In the latter case, regard must be had to the possible presence of all the bodies enumerated in § 192, *a* (**135**); pass on to § 192, 2 (**150**). **137**

1. DETECTION OF THE BASES OF GROUPS III. AND IV. IF PHOSPHATES, &c., OF THE ALKALINE EARTHS ARE NOT PRESENT. **138**

Mix the fluid mentioned at the beginning of the paragraph (**134**); a portion of which you have submitted to a preliminary examination with some chloride of ammonium, then with ammonia, just to alkaline reaction; lastly, with sulphide of ammonium, until the fluid, after being shaken, smells distinctly of that reagent; shake the mixture until the precipitate begins to separate in flakes, and filter.

Keep the FILTRATE,‡ which contains, or may contain, the basis of Groups II. and I., for subsequent examination according to the directions of § 193. Wash the PRECIPITATE with water, to which a very little sulphide of ammonia has been added, and then proceed with it as follows:—

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* If the fluid is colorless, it contains no chromium. If colored, the tint will to some extent act as a guide to the nature of the substance present; thus a green tint, or a violet tint turning green upon boiling, points to the presence of chromium; a light green tint to that of nickel; a reddish color to that of cobalt; the turning yellow of the fluid upon boiling with nitric acid, to that of iron. It must, however, be always borne in mind that these tints are perceptible only if the metallic oxides are present in larger quantity, and also that complementary colors, such as, for instance, the green of the nickel solution and the red of the cobalt solution will destroy each other, and that, accordingly, a solution may contain both metals and yet appear colorless.

† Presence of much chloride of ammonium has a great tendency to prevent the precipitation of borates of the alkaline earths.

‡ If the filtrate has a brownish color, this points to the presence of nickel, sulphide of nickel, as is well known, being slightly soluble in sulphide of ammonium; this, however, involves no modification of the analytical course.

a. IT IS PERFECTLY WHITE; absence of iron, cobalt, nickel. You must test for all the other bases of Groups III. and IV., as the faint tints of sesquioxide of chromium and sulphide of manganese are imperceptible in a large quantity of a white precipitate. Dissolve the precipitate by heating it in a small dish with the least possible amount of hydrochloric acid; boil—should hydrosulphuric acid be evolved—until this gas is completely expelled, concentrate by evaporation, neutralize with carbonate of soda, then add solution of soda in excess, heat to boiling, and keep the mixture for some time in a state of ebullition. **139**

α. The precipitate formed at first dissolves completely in the excess of solution of soda. Absence of manganese and chromium, presence of alumina or oxide of zinc. Test a portion of the alkaline solution with solution of hydrosulphuric acid for ZINC; acidify the remainder with hydrochloric acid, add ammonia *slightly* in excess, and apply heat. The formation of a white, flocculent precipitate shows the presence of ALUMINA. **140**

β. The precipitate formed does not dissolve, or dissolves only partially, in the excess of solution of soda. Filter and test the FILTRATE, as in α (140), for ZINC and ALUMINA. With the undissolved PRECIPITATE proceed as follows:— **141**

aa. If the color of the solution indicates the presence of chromium, fuse the precipitate in the cover of a platinum crucible, together with carbonate and nitrate of soda; treat the fused mass with water, and filter. If the filtrate is yellow, and, after being acidified with acetic acid, gives with acetate of lead a yellow precipitate, CHROMIUM is present.

bb. Test a portion of the precipitate for MANGANESE, by means of the reaction with carbonate of soda in the outer blowpipe flame. If chromium has been found in *aa*, the residue left upon treating the fused mass with water, is used for this purpose.

b. IT IS NOT WHITE; this points to the presence of chromium, manganese, iron, cobalt, or nickel. If it is black, or inclines to black, one of the three metals last-mentioned is present. Under all circumstances, all the oxides of Groups III. and IV. must be looked for. **142**

Remove the washed precipitate from the filter with a spatula, or by rinsing it, with the aid of a washing-bottle, into a test-tube, through a hole made in the bottom of the filter, and pour over it rather dilute cold hydrochloric acid in moderate excess.

α. It dissolves completely (except perhaps a little sulphur, which may separate); absence of cobalt and nickel, at least of notable quantities of these two metals. **143**

Boil until the hydrosulphuric acid is *completely* expelled, filter if particles of sulphur are suspended in the fluid, concentrate by evaporation, neutralize with carbonate of soda, then add solution of potassa or soda in excess, boil, filter the fluid from the insoluble precipitate which is sure to remain,

wash the latter, and proceed first to examine the filtrate, then the precipitate.

aa. Test a portion of the *filtrate* with hydrosulphuric acid for *zinc;* acidify the remainder with hydrochloric acid, and then test it with ammonia for ALUMINA. Compare § 192, 1, *a*, *α* (140). 144

bb. Dissolve a portion of the *precipitate* in hydrochloric acid, and test the solution with sulphocyanide of potassium for IRON. Test other portions for chromium and manganese, according to the directions of § 192, 1, *a*, *β* (141). 145

N. B.—If it is intented to make a very accurate analysis, you have still to subject the remainder of the precipitate mentioned in *bb* (145) to further examination, since it may contain magnesia (thrown down with the alumina); or some other alkaline earths, which may have been carried down along with the sesquioxide of chromium, owing to presence of carbonate of ammonium in the ammonia or sulphide of ammonium; and lastly, also traces of cobalt, nickel, and zinc. Dissolve it, accordingly, in hydrochloric acid, and test the solution for the bodies enumerated, according to the directions of § 192, 2, *b*, *α* and *β* (155 and 156), omitting, however, the addition of sesquioxide of iron, recommended in 156. 146

β. The precipitate is not completely dissolved, a black residue being left; this indicates the presence of cobalt and nickel. Filter, wash the undissolved precipitate, and test the filtrate as directed § 192, 1, *b*, *α* (143); proceed with the residuary precipitate as follows:— 147

aa. Test a portion of it with borax, first in the outer, then in the inner blowpipe-flame. If the bead in the oxidizing flame is violet whilst hot, and of a pale reddish-brown when cold, and turns in the reducing flame gray and turbid, nickel is present; but if the color of the bead is and remains blue, in both flames, and whether hot or cold, COBALT is present. As in the latter case the presence of nickel cannot be distinctly recognised; examine 148

bb. The remainder of the precipitate by incinerating it together with the filter in a coil of platinum wire, heating the ash with some hydrochloric acid, filtering the solution, then evaporating nearly to dryness, and adding nitrite of potassa, and then acetic acid (§ 108, 10). The formation of a yellow precipitate confirms the presence of COBALT. Let the fluid, with the precipitate in it, stand for some time at a gentle heat, then filter, and test the filtrate with solution of soda for nickel. 149

2. DETECTION OF THE BASES OF GROUPS III. AND IV. IN CASES WHERE PHOSPHATES, BORATES, OXALATES, OR SILICATES OF THE ALKALINE EARTHS, OR FLUORIDES OF THE METALS OF THE ALKALINE EARTHS, MAY POSSIBLY HAVE BEEN THROWN DOWN ALONG WITH THESE BASES, *i.e.*, in cases where the original solution was acid, and 150

a precipitate was produced by ammonia in the preliminary examination. See (134).

Mix the fluid mentioned in the beginning of this paragraph (134) with some chloride of ammonium, then with ammonia just to alkaline reaction, lastly with sulphide of ammonium, until the fluid, after being shaken, smells distinctly of this reagent; shake the mixture until the precipitate begins to separate in flakes, and filter. Keep the FILTRATE, which contains, or may contain, the bases of Groups II. and I., for subsequent examination according to the directions of § 193. Wash the precipitate with water to which a very little sulphide of ammonium has been added, and then proceed with it as follows. To give a clear notion of the obstacle to be overcome in this analytical process I must remind you that it is necessary to examine the precipitate for the following bodies: Iron, nickel, cobalt (these show their presence to a certain extent by the black or blackish coloration of the precipitate), manganese, zinc, sesquioxide of chromium (the latter generally reveals its presence by the color of the solution), alumina;—baryta, strontia, lime, magnesia, which latter substances may have fallen down in combination with phosphoric acid, boracic acid, oxalic acid, silicic acid, or in form of fluorides. Besides these bodies, free silicic acid may also be contained in the precipitate as hydrate.

As the original substance must, under all circumstances, be 151
afterwards examined for all acids that might possibly be present, it is not *indispensable* to test for the above enumerated acids at this stage of the analytical process; still, as it is often interesting to know the presence of these acids at once, more especially in cases where a somewhat large proportion of some alkaline earth has been found in the precipitate produced by sulphide of ammonium, a method for the detection of the acids in question will be found appended by way of supplement to the method for the detection of the bases.

Remove the precipitate from the filter with a small spatula, or 152
by rinsing it off with the washing-bottle, and pour over it cold dilute hydrochloric acid in moderate excess.

a. A RESIDUE REMAINS. Filter, and treat the filtrate as 153
directed in *b* (154). The residue, if it is black, may contain sulphide of nickel, and sulphide of cobalt, and besides these, sulphur and silicic acid. Wash, and examine a sample of it in conjunction with phosphate of soda and ammonia before the blowpipe, in the outer flame. If a silica skeleton remains undissolved, (§ 150, 8), this proves the presence of silicic acid. If the color of the bead is blue, COBALT is present; if reddish, turning yellow on cooling, NICKEL. Should the color leave you in doubt, incinerate the filter containing the remainder of the residue, and test for cobalt and nickel by means of nitrite of potassa, as directed § 192, 1, *b*, *β*, *bb* (149).

b. NO RESIDUE IS LEFT (except perhaps a little sulphur, 154
which may separate): absence of nickel and cobalt, at least in any notable proportion.

Boil the solution until the sulphuretted hydrogen is expelled, and then proceed as follows:

a. Mix a small portion of the solution with dilute sulphuric acid. If a precipitate forms, this may consist of sulphates of BARYTA and STRONTIA, possibly also of sulphate of lime. Filter, wash the precipitate, decompose it by boiling or fusion with carbonated alkali, wash the carbonates produced, dissolve them in hydrochloric acid, and test the solution as directed § 193. Mix the fluid which has not been precipitated by dilute sulphuric acid, or the fluid filtered from the precipitate produced, with 3 volumes of spirit of wine. If a precipitate forms, this consists of sulphate of LIME. Filter, dissolve in water, and add oxalate of ammonia to the solution, as a confirmatory proof of the presence of lime. 155

β. Heat a somewhat larger sample with some nitric acid, and test a small portion of the fluid with sulphocyanide of potassium for IRON;* mix the remainder with sesquichloride of iron in sufficient quantity to make a drop of the fluid give a yellowish precipitate† when mixed, on a watch-glass, with a drop of ammonia; concentrate the fluid now until there is only a small quantity left; add to this some water, then a few drops of solution of carbonate of soda, just sufficient to *nearly* neutralize the free acid, and lastly carbonate of baryta in slight excess; stir the mixture, and let it stand in the cold until the fluid above the precipitate has become colorless. Filter now the precipitate (*aa*) from the solution (*bb*), and wash. 156

aa. Boil the *precipitate* for some time with solution of soda, filter, and test the filtrate for ALUMINA,‡ by heating with chloride of ammonium in excess. The part of the precipitate insoluble in solution of soda is examined for CHROMIUM, as directed in § 192, 1, *a*, *β*, *aa* (**141**). 157

bb. Mix the *solution* with some ammonia and sulphide of ammonium.

αα. No precipitate forms: absence of manganese and zinc. Mix the solution containing chloride of barium with dilute sulphuric acid in slight excess, boil, filter, supersaturate with ammonia, and mix with oxalate of ammonia. If a precipitate of oxalate of LIME forms, filter, and test the filtrate with phosphate of soda for MAGNESIA. 158

ββ. A precipitate forms. Filter, and proceed with the filtrate according to the directions of *αα* (**158**). 159

* Whether the iron was present as sesquioxide or as protoxide, must be ascertained by testing the original solution in hydrochloric acid with ferricyanide of potassium and sulphocyanide of potassium.

† The addition of sesquichloride of iron is necessary, to effect the separation of phosphoric acid and silicic acid which may be present.

‡ If the solution contains silicic acid, the precipitate taken for alumina may contain also silicic acid. A simple trial with phosphate of soda and ammonia, on a platinum wire, in the blowpipe flame, will show whether the precipitate really contains silicic acid. Should this be the case, ignite the remainder of the supposed alumina precipitate on the cover of a platinum crucible, add some acid sulphate of potassa, fuse the mixture, and treat the fused mass with water, which will dissolve the alumina, leaving the silicic acid undissolved; precipitate the alumina from the solution by ammonia.

The precipitate may consist of sulphide of manganese and sulphide of zinc, and may contain traces also of sulphide of cobalt and sulphide of nickel. Wash it with water containing some sulphide of ammonium, and then treat it with acetic acid, which will dissolve the sulphide of MANGANESE, if any is present, leaving the other sulphides undissolved. Filter, boil the filtrate with solution of soda, and test the precipitate, which may form, with carbonate of soda in the outer blowpipe flame for MANGANESE. Free the residuary part of the precipitate, which acetic acid has failed to dissolve, by washing, from the acetic acid solution still adhering to it, and then treat it with dilute hydrochloric acid, which will dissolve the *zinc*, if any is present. Filter, add some nitric acid to the filtrate, and concentrate the mixture considerably by boiling; then add to it solution of soda in excess, boil, filter, if necessary, and test the filtrate with sulphide of ammonium for ZINC. Should a precipitate insoluble in solution of soda remain in the last operation, or should the dilute hydrochloric acid have left a black residue, test this precipitate and residue for COBALT and NICKEL, if you have not already previously detected the presence of these bodies; compare § 192, 1, *b*, *β* (**148** and **149**).

γ. If you have found alkaline earths in *α* and *β*, and wish to know the acids in combination with which they have passed into the precipitate produced by sulphide of ammonium, this may be ascertained by making the following experiments with the remainder of the hydrochloric acid solution:— **160**

aa. Test a small portion of it for PHOSPHORIC ACID, by means of molybdic acid (§ 143, 11). **161**

bb. Mix another portion with carbonate of soda *in excess*, boil for some time, filter, and test one-half of the filtrate for OXALIC ACID, by acidifying it with acetic acid, and adding solution of sulphate of lime; the other half for BORACIC ACID, by slightly acidifying it with hydrochloric acid, and testing with turmeric paper (§ 145 and § 146).

cc. Evaporate a third portion in a small dish or in a watch-glass, dry the residue thoroughly, and then treat with hydrochloric acid. If there was any SILICIC ACID in the solution, this will be left undissolved. **162**

dd. Precipitate the remainder with ammonia, filter, wash and dry the precipitate, and examine it for FLUORINE according to § 147, 5.

§ 193.

(*Separation and Detection of the Oxides of Group II., which are precipitated by Carbonate of Ammonia in Presence of Chloride of Ammonium, viz., Baryta, Strontia, Lime*).

TO A SMALL PORTION OF THE FLUID IN WHICH AMMONIA AND

SULPHIDE OF AMMONIUM HAVE FAILED TO PRODUCE A PRECIPITATE, OR OF THE FLUID FILTERED FROM THE PRECIPITATE FORMED, ADD CHLORIDE OF AMMONIUM, IF THE SOLUTION CONTAINS NO AMMONIACAL SALT, THEN CARBONATE OF AMMONIA AND SOME CAUSTIC AMMONIA, AND HEAT FOR SOME TIME VERY GENTLY (not to boiling).

1. NO PRECIPITATE FORMS: absence of any notable quantity of baryta, strontia, and lime. Traces of these alkaline earths may, however, be present; to detect them, add to another portion of the fluid some sulphate of ammonia (prepared by supersaturating dilute sulphuric acid with ammonia): if the fluid becomes turbid, it contains traces of BARYTA; add to a third portion some oxalate of ammonia; if the fluid turns turbid—which reaction may perhaps require some time to manifest itself—traces of lime are present. Treat the remainder of the fluid as directed § 194, after having previously removed the traces of lime and baryta which may have been found, by means of the reagents that have served to effect their detection. 163

2. A PRECIPITATE IS FORMED. Presence of LIME, BARYTA, or STRONTIA. Filter, test portions of the filtrate with sulphate and oxalate of ammonia, for traces of lime and baryta, which it may possibly still contain, remove such traces, should they be found, by means of the said reagents, and examine the fluid, thus perfectly freed from baryta, strontia, and lime, for magnesia according to the directions of § 194. Wash the precipitate produced by carbonate of ammonia, dissolve it in the least possible amount of dilute hydrochloric acid, and add to a small portion of the fluid some *solution of sulphate of lime* (not too little). 164

a. No precipitate is formed, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of baryta and strontia; presence of LIME. To remove all doubt, mix another sample with oxalate of ammonia.

b. A precipitate is formed by solution of sulphate of lime.

α. It is formed immediately; this indicates BARYTA. Besides this, strontia and lime may also be present. 165

Evaporate the remainder of the hydrochloric acid solution of the precipitate produced by carbonate of ammonia to dryness, digest the residue with strong alcohol, decant the fluid from the undissolved chloride of barium, dilute with an equal volume of water, mix with a few drops of hydrofluosilicic acid—which throws down the small portion of baryta that had dissolved in form of chloride of barium—allow the mixture to stand for some time; filter, evaporate the alcoholic solution to dryness, dissolve the residue in water, and test a portion of the fluid with a dilute solution of sulphate of potassa (§ 96, 3). If a precipitate forms immediately, or in the course of half an hour, the presence of STRONTIA is demonstrated. In that case, let the fluid with the precipitate in it stand at rest for some time, then filter, and add ammonia and oxalate of ammonia to the filtrate. The formation of a white precipitate indicates LIME. If sulphate of potassa has failed to produce a precipitate, the remainder of the solution of the residue left upon evapora-

tion of the alcoholic fluid is tested at once with ammonia and oxalate of ammonia for lime.

β. *It is formed only after some time.* Absence of baryta, presence of STRONTIA. Mix the remainder of the hydrochloric acid solution with sulphate of potassa, let the mixture stand for some time, then filter, and test the filtrate with ammonia and oxalate of ammonia for LIME. 166

§ 194.

(*Examination for Magnesia.*)

TO A PORTION OF THE FLUID IN WHICH CARBONATE, SULPHATE, AND OXALATE OF AMMONIA HAVE FAILED TO PRODUCE A PRECIPITATE (§ 193, 1 [163]), OR OF THE FLUID FILTERED FROM THE PRECIPITATES FORMED (§ 193, 2 [164]), ADD AMMONIA, THEN SOME PHOSPHATE OF SODA, AND, SHOULD A PRECIPITATE NOT AT ONCE FORM, RUB THE INNER SIDES OF THE VESSEL WITH A GLASS ROD, AND THEN LET THE MIXTURE STAND FOR SOME TIME.

1. NO PRECIPITATE IS FORMED: absence of magnesia. Evaporate another portion of the fluid to dryness,* and ignite gently. *If a residue remains,* treat the remainder of the fluid the same as the sample, and examine the residue, which by the moderate ignition to which it has been subjected has been freed from ammonia, for potassa and soda, according to the directions of § 195.—*If no residue is left,* this is a proof of the absence of the fixed alkalies; pass on to § 196. 167

2. A PRECIPITATE IS FORMED: presence of MAGNESIA. As testing for alkalies can proceed with certainty only after the removal of magnesia, evaporate the remainder of the fluid to dryness, and ignite until all ammoniacal salts are removed. Warm the residue with water, add baryta-water, prepared from the crystals, as long as a precipitate continues to form, boil, filter, add to the filtrate a mixture of carbonate of ammonia with some caustic ammonia in slight excess, heat for some time gently, filter, evaporate the filtrate to dryness, adding some chloride of ammonium during the process (to convert into chlorides the caustic alkalies that may have formed), ignite the residue gently, then dissolve it in a little water, precipitate, if necessary, once more, with ammonia and carbonate of ammonia, evaporate again, and if a residue remains, ignite this gently, and finally examine it according to the directions of § 195. 168

§ 195.

(*Examination for Potassa and Soda.*)

YOU HAVE NOW TO EXAMINE FOR POTASSA AND SODA THE GENTLY IGNITED RESIDUE, FREE FROM SALTS OF AMMONIA AND ALKALINE EARTHS, WHICH HAS BEEN OBTAINED IN § 194, 1 (167), OR IN § 194, 2 (168).

Dissolve it in a little water, filter, if necessary, evaporate until

* The most convenient way is to conduct the evaporation in the cover of a platinum crucible.

there is only a small quantity of fluid left, and transfer one-half of this to a watch-glass, leaving the other half in the porcelain dish.

1. To the one-half in the porcelain dish add, after cooling, a few drops of solution of *bichloride of platinum*. If a yellow, crystalline precipitate forms immediately, or after some time, POTASSA is present. Should no precipitate form, evaporate to dryness at a gentle heat, and treat the residue with a very small quantity of water or, if chlorides alone are present, with a mixture of water and alcohol, when the presence of minute traces of potassa will be revealed by a small quantity of a heavy yellow powder being left undissolved. 169

2. To the other half of the fluid (in the watch-glass) add some *antimonate of potassa*. If this produces at once or after some time a crystalline precipitate, SODA is present. If the quantity of soda present is only very trifling, it often takes twelve hours before minute crystals of antimonate of soda will separate; you must therefore always wait full that time for the possible manifestation of the reaction, before deciding, from its non-appearance, that no soda is present. As regards the form of the crystals, consult § 91. 170

§ 196.

(*Examination for Ammonia.*)

There remains still the examination for ammonia. Triturate some of the body under examination, or, if a fluid, a portion of the latter, together with an excess of hydrate of lime, and, if necessary, a little water. If the escaping gas smells of ammonia, if it restores the blue color of reddened litmus paper, and forms white fumes with hydrochloric acid vapors, brought into contact with it by means of a glass rod, AMMONIA is present. The reaction is the most sensitive, if the trituration is made in a small beaker, and the latter covered with a glass plate with a slip of moistened turmeric or moist reddened litmus paper adhering to the under side. 171

Complex Compounds.

A, 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.*

I. *In the Absence of Organic Acids.*

§ 197.

Consider, in the first place, *which* are the acids that form with the bases found compounds soluble in water, and let this guide you in the examination. To students the table given in Appendix IV. will prove of considerable assistance.

1. The ACIDS of ARSENIC, as well as CARBONIC ACID, HYDROSULPHURIC ACID, CHROMIC ACID, and SILICIC ACID, have generally been detected already in the course of testing for the bases; compare also § 181, 1 and 2. 172

* Consult also Section III.

2. Add to a portion of the solution chloride of barium or, if lead, silver, or suboxide of mercury are present, nitrate of baryta, and, should the reaction of the fluid be acid, add ammonia to neutral or slightly alkaline reaction.

a. NO PRECIPITATE IS FORMED: absence of sulphuric acid, 173 phosphoric acid, chromic acid, silicic acid, oxalic acid, arsenious and arsenic acids, as well as of notable quantities of boracic acid and hydrofluoric acid.* Pass on to 3 (175).

b. A PRECIPITATE IS FORMED. Dilute the fluid, and add 174 hydrochloric acid; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present.

3. Add nitrate of silver to a portion of the solution. If this fails 175 to produce a precipitate, test the reaction, and add to the fluid, if it is acid, some dilute ammonia, taking care to add the reagent so gently and cautiously that the two fluids do not intermix; if the reaction is alkaline, on the other hand, add with the same care some dilute nitric acid, instead of ammonia, and watch attentively whether a precipitate or a cloud forms in the layer between the two fluids.

a. NO PRECIPITATE IS FORMED IN THE LAYER BETWEEN THE 176 TWO FLUIDS, NEITHER IMMEDIATELY NOR AFTER SOME TIME. Pass on to 4 (181); there is neither chlorine, bromine, iodine, cyanogen,† ferro- and ferricyanogen present, nor sulphur; nor phosphoric acid, arsenic acid, arsenious acid, chromic acid, silicic acid, oxalic acid; nor boracic acid, if the solution was not too dilute.

b. A PRECIPITATE IS FORMED. Observe the color‡ of it, 177 then add nitric acid, and shake the mixture.

α. The precipitate redissolves completely: absence of chlorine, bromine, iodine, cyanogen, ferro- and ferricyanogen, and also of sulphur. Pass on to 4 (181).

β. A residue is left: chlorine, bromine, iodine, cyanogen, 178 ferro- or ferricyanogen may be present; and if the residue is black or blackish, HYDROSULPHURIC ACID or a soluble METALLIC SULPHIDE.—The presence of sulphur may, if necessary, be readily established beyond doubt, by mixing another portion of the solution with some solution of sulphate of copper.

aa. Test another portion of the fluid for IODINE, and subsequently for BROMINE, by the methods described in § 157.

bb. Test a small portion of the fluid with sesqui- 179 chloride of iron for FERROCYANOGEN; and, if the color of the silver precipitate leads you to suspect the presence of

* If the solution contains an ammoniacal salt in somewhat considerable proportion, the non-formation of a precipitate cannot be considered a conclusive proof of the absence of these acids, since the baryta salts of most of them (not the sulphate), are, in presence of ammoniacal salts, more or less soluble in water.

† That the cyanogen in cyanide of mercury is not indicated by nitrate of silver has been mentioned § 181, 5 (73).

‡ Chloride, bromide, cyanide, and ferrocyanide of silver, and oxalate, silicate, and borate of silver are white; iodide of silver, tribasic phosphate, and arsenite of silver are yellow; arsenate of silver and ferricyanide of silver are brownish-red; chromate of silver is purple-red; sulphide of silver black.

FERRICYANOGEN, test another portion for this latter substance with sulphate of iron.—If the original solution has an alkaline reaction, some hydrochloric acid must be added before the addition of the sesquichloride of iron, or the sulphate of iron.

cc. CYANOGEN, if present in form of a simple metallic cyanide soluble in water, may usually be readily recognised by the smell of hydrocyanic acid which the body under examination emits, and which is rendered more strongly perceptible by addition of a little dilute sulphuric acid.—If no ferrocyanogen is present, the presence of cyanogen may be ascertained by the method given in § 155, 6.

dd. Should bromine, iodine, cyanogen, ferrocyanogen, 180
ferricyanogen, and sulphur not be present, the precipitate which nitric acid has failed to dissolve, consists of CHLORIDE of silver.

However, should the analytical process have revealed the presence of any of the other bodies, a special examination for chlorine may become necessary, viz., in cases where the *quantity* of the precipitate will not enable the operator to pronounce with positive certainty on the presence or absence of the latter element.* In such cases, which are of rare occurrence, however, the method given in § 157 is resorted to.

4. Test another portion for NITRIC ACID, by means of sulphate of 181
iron and sulphuric acid (§ 159).

5. To ascertain whether CHLORIC ACID is present, pour a little concentrated sulphuric acid over a small sample of the solid body under examination: ensuing yellow coloration of the acid resolves the question in the affirmative (§ 160). You have still to test for phosphoric acid, boracic acid, silicic acid, oxalic acid, and chromic acid, as well as for hydrofluoric acid. For the first five acids test only in cases where both chloride of barium and nitrate of silver have produced precipitates in neutral solutions. Compare also foot note to § 197, 2, *a.*

6. Test for PHOSPHORIC ACID, by adding to a portion of the fluid 182
ammonia in excess, then chloride of ammonium and sulphate of magnesia (§ 143, 7). Very minute quantities of phosphoric acid are detected most readily by means of molybdic acid (§ 143, 11).

7. To effect the detection of OXALIC ACID and HYDROFLUORIC ACID, add chloride of calcium to a portion of the solution. If this produces a precipitate which is not redissolved by addition of acetic acid, one or both bodies are present. Examine therefore now a sample of the original substance for fluorine, according to the directions of § 147, 5, another sample for oxalic acid, by the method given in § 146, 7.

8. Acidulate a portion of the fluid slightly with hydrochloric 183

* Supposing, for instance, the solution of nitrate of silver to have produced a copious precipitate insoluble in nitric acid, and the subsequent examination to have shown mere traces of iodine and bromine, the presence of chlorine may be held to be demonstrated without requiring additional proof.

acid, and then test for BORACIC ACID, by means of turmeric paper (§ 145).

9. Should SILICIC ACID not yet have been found in the course of testing for the bases, acidulate a portion of the fluid with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid (§ 150, 3).

10. CHROMIC ACID is readily recognised by the yellow or red color of the solution, and by the purple-red color of the precipitate produced by nitrate of silver.—If there remains the least doubt on the point, test for chromic acid with acetate of lead and acetic acid (§ 138).

Complex Compounds.

A, 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.

II. *In Presence of Organic Acids.*

§ 198.

1. The examination for inorganic acids, inclusive of oxalic acid, 184
is made in the manner described in § 197. As the tartrates and citrates of baryta and oxide of silver are insoluble in water, tartaric acid and citric acid can be present only in cases where both chloride of barium and nitrate of silver have produced precipitates in the neutral fluid; still, in drawing a conclusion, you must bear in mind that the said salts are slightly soluble in solutions of salts of ammonia.

The examination for the organic acids is conducted as follows:—

2. Make a portion of the fluid feebly alkaline by addition of am- 185
monia, filter, if necessary, add some chloride of ammonium, then chloride of calcium, shake vigorously, and let the mixture stand at rest from ten to twenty minutes.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of tartaric acid; pass on to 3.

b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER SOME 186
TIME. Filter, wash, and keep the filtrate for further examination according to the directions of 3.

Digest and shake the precipitate with solution of soda, without applying heat, then dilute with a little water, filter, and boil the filtrate some time. If a precipitate separates, TARTARIC ACID may be assumed to be present. Filter hot, and subject the precipitate to the ammonia and nitrate of silver test described in § 162, 8.

3. Mix the fluid in which chloride of calcium has failed to produce a precipitate, or that which has been filtered from the precipitate—in which latter case some more chloride of calcium is to be added—with alcohol.

a. NO PRECIPITATE IS FORMED. Absence of citric acid and 187
malic acid. Pass on to 4.

b. A PRECIPITATE IS FORMED. Filter and treat the filtrate 188
as directed in 4. As regards the precipitate, treat this as follows:—

After washing with some alcohol, dissolve on the filter in a little dilute hydrochloric acid, add ammonia to the filtrate to feebly alkaline reaction, and then boil for some time.

α. THE FILTRATE REMAINS CLEAR. Absence of citric acid. Probable presence of MALIC ACID. Add alcohol again to the fluid, and test the lime precipitate in the manner directed § 165, to make sure whether malic acid is really present or not.

189 *β.* A HEAVY, WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. Filter boiling, and test the filtrate for malic acid in the same manner as in *α.* To remove all doubt as to whether the precipitate is citrate of lime or not, it is advisable to dissolve once more in some hydrochloric acid, to supersaturate again with ammonia, and to boil; if the precipitate really consisted of citrate of lime, it will now be thrown down again. (Compare § 164, 3.)

190 4. Heat the filtrate of 3, *b* (**188**) (or the fluid in which addition of alcohol has failed to produce a precipitate, 3, *a* [**187**]), to expel the alcohol, neutralize *exactly* with hydrochloric acid, and add sesquichloride of iron. If this fails to produce a light brown, flocculent precipitate, neither succinic nor benzoic acid is present. If a precipitate of the kind is formed, filter, digest, and heat the washed precipitate with ammonia in excess; filter, evaporate the filtrate nearly to dryness, and test a portion for SUCCINIC ACID with chloride of barium and alcohol; the remainder for BENZOIC ACID with hydrochloric acid (§ 169). Benzoic acid may generally be readily detected also in the original substance, by pouring some dilute hydrochloric acid over a small portion of the latter, which will leave the benzoic acid undissolved; it is then filtered and heated on platinum foil (§ 168, 1).

191 5. Evaporate a portion of the solution to dryness—if acid, after previous saturation with soda—introduce the residue, or a portion of the original dry substance into a small tube, pour some alcohol over it, add about an equal volume of concentrated sulphuric acid, and heat to boiling. Evolution of the odor of acetic ether demonstrates the presence of ACETIC ACID. This odor is rendered more distinctly perceptible by shaking the cooling or cold mixture.

192 6. To effect the detection of FORMIC ACID, add to a portion of the solution nitrate of silver in not too small a proportion, then soda until the fluid is *exactly* neutralized, and boil. If formic acid is present, reduction of the silver to the metallic state ensues (§ 171, 4). The reaction with nitrate of suboxide of mercury may be had recourse to as a conclusive test (§ 171, 4).*

* In presence of chromic acid the reduction of oxide of silver and of suboxide of mercury is not a positive proof of the presence of formic acid. In cases where the two acids are present, the following method must be resorted to:—Mix the original solution with some nitric acid, add oxide of lead in excess, shake the mixture, filter, add to the filtrate dilute sulphuric acid in excess, and distil. Test the distillate as directed § 172. In presence of tartaric acid also it is the safest way to distil the formic acid first, with addition of dilute sulphuric acid.

Complex Compounds.

A, 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

DETECTION OF THE ACIDS.

I. *In the Absence of Organic Acids.*

§ 199.

In the examination of these compounds attention must be directed to all acids, with the exception of chloric acid. Cyanogen compounds and silicates are not examined by this method. (Compare § 202 and § 203.)

1. CARBONIC ACID, SULPHUR (in form of metallic sulphides), ARSE- **193**
NIOUS ACID, ARSENIC ACID, and CHROMIC ACID, if present, have been found already in the course of the examination for bases; NITRIC ACID, if present, has been detected in the course of the preliminary examination, by the ignition of the powdered substance in a glass tube (§ 174).

2. Mix a sample of the substance with 4 parts of pure carbonate **194**
of soda and potassa, and, should it contain a metallic sulphide, add some nitrate of soda; fuse the mixture in a platinum crucible if there are no reducible metals present, in a porcelain crucible if reducible metals are present; boil the fused mass with water, and add a little nitric acid, leaving the reaction of the fluid, however, still alkaline; heat again, filter, and proceed with the filtrate according to the directions of § 197, to effect the detection of all the acids which were combined with the bases.*

3. As the phosphates of the alkaline earths are only incompletely **195**
decomposed by fusion in conjunction with carbonate of soda and potassa, it is always advisable in cases where alkaline earths are present, and phosphoric acid has not yet been detected, to dissolve a fresh sample of the body under examination in hydrochloric acid or nitric acid, and test the solution for PHOSPHORIC ACID with molybdic acid.

4. If in the course of the examination for bases, alkaline earths have been found, it is also advisable to test a separate portion of the body under examination for FLUORINE, by the method described in § 147, 5.

5. That portion of the substance under examination which is **196**
treated of in § 199, 2 (**194**), can be tested for SILICIC ACID only in cases where the fusion has been effected in a platinum crucible; in cases where a porcelain crucible has been used, it is necessary to examine a separate portion of the body for silicic acid, by evaporating the hydrochloric or nitric acid solution.

6. Examine a separate sample of the body for OXALIC ACID as directed in § 200, 3.

* If the body examined has been found to contain a metallic sulphide, a separate portion of it must be examined for sulphuric acid, by heating it with hydrochloric acid, filtering, adding water to the filtrate, and then testing the fluid with chloride of barium.

Complex Compounds.

A, 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

DETECTION OF THE ACIDS.

II. *In Presence of Organic Acids.*

§ 200.

1. Conduct the examination for inorganic acids according to the direction of § 199. **197**

2. Test for ACETIC ACID as directed § 198, *5* (**191**).

3. Dissolve a portion of the compound under examination in the least possible amount of hydrochloric acid, filter, if necessary, and test the undissolved residue which may be left, for BENZOIC ACID by application of heat; add to the filtrate solution of carbonate of soda in considerable excess, and, besides this, also a little solid carbonate of soda, boil the mixture for a few minutes, and then filter the fluid from the precipitate. In the filtrate you have now all the organic acids in solution, combined with soda. Acidify the filtrate with hydrochloric acid, heat, and proceed according to the direction of § 198. **198**

Complex Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE BOTH IN WATER AND IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

DETECTION OF THE BASES, ACIDS, AND NON-METALLIC ELEMENTS.

§ 201.

To this class belong the following bodies and compounds. **199**

SULPHATE OF BARYTA, SULPHATE OF STRONTIA, and SULPHATE OF LIME.*

SULPHATE OF LEAD† and chloride of lead.‡

CHLORIDE OF SILVER, bromide of silver, iodide of silver, cyanide of silver,|| ferro- and ferricyanide of silver.¶

SILICIC ACID and many SILICATES.

Native alumina, or alumina which has passed through a process of intense ignition, and many aluminates.

Ignited sesquioxide of chromium and chrome-ironstone (a compound of sesquioxide of chromium and protoxide of iron).

* Sulphate of lime passes partially into the solution effected by water, and often completely into that effected by acids.

† Sulphate of lead may pass completely into the solution effected by acids.

‡ Chloride of lead can here only be found if the precipitate insoluble in acids has not been thoroughly washed with hot water.

|| Bromide, iodide, and cyanide of silver are decomposed by boiling with nitrohydrochloric acid, and converted into chloride of silver; they can accordingly be found here only in cases where the operator has to deal with a substance which—as nitrohydrochloric acid has failed to effect its solution—is examined directly by the method described in this paragraph (§ 201).

¶ With regard to the examination of these compounds, compare also § 202.

Ignited, and native binoxide of tin (tin-stone).
Some metaphosphates and some arsenates.
FLUORIDE OF CALCIUM and a few other compounds of fluorine.
SULPHUR.
CARBON.

Of these compounds those printed in small capitals are more frequently met with. As the silicates perform a highly important part in mineral analysis, a special chapter (§ 203—§ 206) is devoted to them.

The substance under examination which is insoluble in water and in acids is in the first place subjected to the preliminary experiments here described in *a—e*, if the quantity at your disposal is not absolutely too small to admit of this proceeding; in cases where the quantity is insufficient for the purpose, the operator must omit this preliminary examination, and at once pass on to 1, bearing in mind, however, that the body may contain *all* the aforesaid substances and compounds.

a. Examine closely and attentively the physical state and con- 200
dition of the substance, to ascertain whether you have to deal with a homogeneous mass or with a mass composed of dissimilar particles; whether the body is sandy or pulverulent, whether it has the same color throughout, or is made up of variously-colored particles, &c. The microscope, or even a simple magnifying glass, will be found very useful at this stage of the examination.

b. Heat a small sample in a glass tube sealed at one end. If 201
brown fumes arise, and SULPHUR sublimes, this is of course a proof of the presence of that substance.

c. If the substance is black, this indicates, in most cases, the pre- 202
sence of carbon (wood-charcoal, pit-coal, bone-black, lamp-black, graphite, &c). Heat a small sample on platinum foil over the blowpipe flame; if the substance which blackens the fingers is consumed, this may be held to be a positive proof of the presence of CARBON in some shape or other. Graphite, which may be readily recognised by its property of communicating its blackish-gray color to the fingers, to paper, &c., requires the application of oxygen for its easy combustion.

d. Warm a small sample, together with a small lump of cyanide 203
of potassium and some water, for some time, filter, and test the filtrate with sulphide of ammonium. The formation of a brownish-black precipitate shows that the substance under examination contains a compound of SILVER.

e. If an undissolved residue has been left in *d*, wash this tho- 204
roughly with water, and, if white, sprinkle a few drops of sulphide of ammonium over it; if it turns black, salts of LEAD are present. If, however, the residue left in *d* is black, heat it with some acetate of ammonia, adding a few drops of acetic acid, filter, and test the filtrate for LEAD, by means of sulphuric acid and hydrosulphuric acid.*

The results obtained by these preliminary experiments serve to guide the operator now in his further course of proceeding.

* The presence of lead in silicates, *e.g.* in glass containing lead, cannot be detected by this method.

1, *a*. SALTS OF LEAD ARE NOT PRESENT. Pass on to 2 (**206**). **205**

b. SALTS OF LEAD ARE PRESENT. Heat the substance repeatedly with a concentrated solution of acetate of ammonia, until the salt of lead is completely dissolved out. Test a portion of the filtrate for CHLORINE, another for SULPHURIC ACID, and the remainder for LEAD, by addition of sulphuric acid in excess, and by hydrosulphuric acid. If acetate of ammonia has left a residue, wash this, and treat it as directed in 2.

2, *a*. SALTS OF SILVER ARE NOT PRESENT. Pass on to 3. **206**

b. SALTS OF SILVER ARE PRESENT. Digest the substance free from lead, or which has been freed from that metal by acetate of ammonia, repeatedly with cyanide of potassium and water, at a gentle heat (in presence of sulphur, in the cold), until all the salt of silver is removed. If an undissolved residue is left, wash this, and then proceed with it according to the directions of 3 (**207**). Of the *filtrate*, which contains cyanide of potassium, mix the larger portion with sulphide of ammonium, to precipitate the silver. Wash the precipitated sulphide of silver, then dissolve it in nitric acid, dilute the solution, and add hydrochloric acid, to ascertain whether the precipitate really consisted of sulphide of silver. Test another small portion of the filtrate for SULPHURIC ACID.*

3, *a*. SULPHUR IS NOT PRESENT. Pass on to 4. **207**

b. SULPHUR IS PRESENT. Heat the substance free from silver and lead in a covered porcelain crucible until all the sulphur is expelled, and, if a residue is left, treat this according to the directions of 4 (**208**).

4. Mix the substance free from silver, lead, and sulphur with **208**
2 parts of carbonate of soda, 2 parts of carbonate of potassa, and 1 part of nitrate of potassa,† heat the mixture in a platinum crucible until the mass is in a state of calm fusion, place the red hot crucible on a thick, cold iron plate, and let it cool. By this means you will generally succeed in removing the fused mass from the crucible in an unbroken lump. Soak the mass now in water, boil, filter, and wash the residue until chloride of barium no longer produces a precipitate in the washings. (Add only the first washings to the filtrate.)

a. *The solution obtained* contains the acids which were **209**
present in the substance decomposed by fluxing (**208**). But it may, besides these acids, contain also such bases as are soluble in caustic alkalies. Proceed as follows :—

α. Test a small portion of the solution for SULPHURIC ACID.

β. Test another portion with molybdic acid for PHOSPHORIC ACID and ARSENIC ACID. If a yellow precipitate

* As the carbonate of potassa contained in the cyanide of potassium may have produced a total or partial decomposition of any sulphates of the alkaline earths which happened to be present.

† Addition of nitrate of potassa is useful even in the case of white powders, as it counteracts the injurious action of silicate of lead, should any be present, upon the platinum crucible. In the case of black powders, the proportion of nitrate of potassa must be correspondingly increased, in order that carbon, if present, may be consumed as completely as possible, and that any chrome-ironstone existing in the compound, may be more thoroughly decomposed.

forms, remove the arsenic acid which may be present with hydrosulphuric acid, and then test once more for phosphoric acid.

γ. Test another portion for FLUORINE (§ 147, 7).

δ. If the solution is yellow, CHROMIC ACID is present. To remove all doubt on the point, acidify a portion of the solution with acetic acid, and test with acetate of lead.

ε. Acidify the remainder of the solution with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid and water. If a residue is left which refuses to dissolve even in boiling water, this consists of SILICIC ACID. Test the hydrochloric acid solution now in the usual way for those bases which, being soluble in caustic alkalies, may be present. **210**

b. Dissolve the residue left in 4 (**208**) in hydrochloric acid (effervescence indicates the presence of alkaline earths), and test the solution for the bases as directed in § 188. (If much silicic acid has been found in ε (**210**), it is advisable to evaporate the solution of the residue to dryness, and to treat the residuary mass with hydrochloric acid and water, in order that the silicic acid remaining may also be removed as completely as possible.) **211**

5. If you have found in 4 that the residue insoluble in acids contains a silicate, treat a separate portion of it according to the directions of § 205, 2 (**228**), to ascertain whether or not this silicate contains alkalies. **212**

6. If a residue is still left undissolved upon treating the residue left in 4 with hydrochloric acid (**211**), this may consist either of silicic acid, which has separated, or of an undecomposed portion of sulphate of baryta; it may, however, also be fluoride of calcium, and if it is dark-colored, chrome-ironstone, as the last-named two compounds are only with difficulty decomposed by the method given in 4. I would therefore remind the student that fluoride of calcium may be readily decomposed by means of sulphuric acid; and, as regards the decomposition of chrome-ironstone, I can recommend the following method, first proposed by *Hart*: Project the fine powder into 8 times the quantity of fused borax, stir the mixture frequently, and keep the crucible for half-an-hour at a bright red heat. Add now to the fusing mass carbonate of soda so long as effervescence continues, and then finally add 3 times the weight of the chrome-ironstone of a mixture of equal parts of carbonate of soda and nitrate of potassa, whilst actively stirring the mixture with a platinum wire. Let the mass cool, and, when cold, boil it with water. **213**

7. If the residue insoluble in acids contained silver, you have still to ascertain whether that metal was present in the original substance as chloride, bromide, iodide, &c., of silver, or whether it has been converted into the form of chloride of silver by the treatment employed to effect the solution of the original substance. For that purpose, treat a portion of the original substance with boiling water until the soluble part is completely removed; then treat the residuary portion in the same way with dilute nitric acid, wash the undissolved residue with water, and test a small **214**

sample of it for silver according to the directions of § 201, *d* (**203**). If silver is present, proceed to ascertain the salt-radical with which the metal is combined; this may easily be effected by boiling the remainder of the residue in the first place with rather dilute solution of soda, filtering, and testing the filtrate, after acidifying it, for ferro- and ferricyanogen. Digest the washed residue now with finely granulated zinc and water, with addition of some sulphuric acid, and filter after the lapse of ten minutes. You may now at once test the filtrate for chlorine, bromine, iodine, and cyanogen; or you may first throw down the zinc with carbonate of soda, in order to obtain the salt-radicals in combination with sodium.

SECTION II.

PRACTICAL COURSE

IN PARTICULAR CASES.

I. Special Method of effecting the Analysis of Cyanides, Ferrocyanides, etc., insoluble in Water, and also of insoluble mixed Substances containing such Compounds.*

§ 202.

The analysis of ferrocyanides, ferricyanides, &c., by the common method is often attended by the manifestation of such anomalous reactions as easily to mislead the analyst. Moreover, acids often fail to effect their complete solution. For these reasons it is advisable to analyze them, and mixtures containing such compounds, by the following special method:— **215**

Treat the substance with water until the soluble parts are entirely removed, and boil the residue with strong solution of potassa or soda; after a few minutes ebullition add some carbonate of soda, and boil again for some time; filter, should a residue remain, and wash the latter.

1. The *residue*, if any has been left, is now free from cyanogen, unless the substance under examination contains cyanide of silver, in which case the residue would of course still contain cyanogen. Examine the residue now by the common method, beginning at § 178, 2 (**34**). **216**

2. The *solution* or *filtrate*, which, if combinations of compound cyanogen radicals were originally present, contains these combined with alkali metals, may also contain other acids, which have been separated from their bases by the process of boiling with carbonate of soda, and lastly also, such oxides as are soluble in caustic alkalies. **217**

* Before entering upon this course of analysis, consult the special remarks to the paragraph (§ 202), page 274, in the Third Section.

Treat the solution as follows:—

a. Mix the alkaline fluid with a sufficient quantity of hydrosulphuric acid. 218

α. *No permanent precipitate is formed.* Absence of zinc and lead. Pass on to *b*.

β. *A permanent precipitate is formed.* Add to the fluid a little yellow sulphide of sodium, heat moderately, filter, wash the precipitate, and treat the filtrate as directed in *b*. Dissolve the washed precipitate in nitric acid, and examine the solution for copper, lead, zinc, and other metals of the fourth group, which may, in the same way as copper, have passed into the alkaline solution, by the agency of organic matters.

b. Mix the alkaline fluid, which contains now also sulphide 219
of an alkali metal, with nitric acid to acid reaction, and, if necessary, add once more hydrosulphuric acid.

α. *No precipitate is formed.* Absence of mercury and of the oxides of the sixth group. Pass on to *c*.

β. *A precipitate is formed.* Filter, wash the precipitate, and then examine it for mercury, and the metals of the sixth group, according to the directions of § 189.

c. The fluid, acidified with nitric acid, and therefore abun- 220
dantly supplied with nitrates of alkalies, may still contain the metals which, in combination with cyanogen, form compound radicals (iron, cobalt, manganese, chromium), and, besides these, also alumina. You have to test it also for cyanogen, respectively, ferrocyanogen, cobalticyanogen, &c., and for other acids. Divide it, therefore, into two portions, α and β. Examine α for the acids according to the directions of § 197. (Cobalticyanide may be recognised as such by its giving with salts of nickel greenish, with salts of manganese and zinc white precipitates.)

Evaporate β to dryness, and heat the residue to fusion. Pour the fused mass upon a piece of porcelain, boil with water, filter, and examine the residue for IRON, MANGANESE, COBALT, and ALUMINA. Test a portion of the filtrate (if yellow) for CHROMIC ACID, the remainder for ALUMINA—which may have passed partially or completely into the solution, through the agency of the caustic alkalies formed, in the process of fusion, from the nitrates of the alkalies present.

II. Analysis of Silicates.

§ 203.

Whether the body to be analyzed is a silicate, or contains one, is 221
ascertained by the preliminary examination with phosphate of soda and ammonia before the blowpipe; since, in the process of fusion, the metallic oxides dissolve, whilst the separated silicic acid floats about in the liquid bead as a transparent, swollen mass.

The analysis of the silicates differs, strictly speaking, from the common course only in so far as the preliminary treatment is concerned, which is required to effect the separation of the silicic acid from the bases, and to obtain the latter in solution.

The silicates and double silicates are divided into two distinct classes, which require respectively a different method of analysis; viz., (1) silicates decomposable by acids (hydrochloric acid, nitric acid, sulphuric acid) and (2) silicates which are not decomposed by acids.

To ascertain to which of these two classes a silicate belongs, reduce it to a very fine powder, and digest a portion with hydrochloric acid at a temperature near the boiling point. If this fails to decompose it, try another portion with tolerably concentrated sulphuric acid, and apply heat. If this also fails, after some time, to produce the desired effect, the silicate belongs to the second class. Whether decomposition has been effected by the acid or not may generally be learned from external indications, as a colored solution forms almost invariably, and the separated gelatinous, flocculent, or finely-pulverulent hydrate of silicic acid takes the place of the original heavy powder which grated under the glass rod with which it was stirred; the separated hydrate of silicic acid will, after filtering and washing, dissolve in boiling solution of potassa or soda, which affords an additional means of identification.

Before proceeding further, test a portion of the pulverized compound also for water, by heating it in a perfectly dry glass tube. If the substance contains hygroscopic moisture it must first be dried by protracted exposure to a temperature of 212° F. Apply a gentle heat at first, but ultimately an intense heat, by means of the blowpipe; you may also conveniently combine with this a preliminary examination for fluorine (§ 147, 8).

A. Silicates decomposable by Acids.

§ 204.

*a. Silicates decomposable by hydrochloric acid or by nitric acid.**

1. Digest the finely pulverized silicate with hydrochloric acid at 222
a temperature near the boiling point, until complete decomposition is effected, filter off a small portion of the fluid, evaporate the remainder, together with the silicic acid suspended therein, to dryness, and expose the residue to a temperature somewhat exceeding 212° F., with constant stirring, until no more, or very few, hydrochloric acid fumes escape; allow it to cool, moisten the residue with hydrochloric acid, or as the case may be, with nitric acid, afterwards add a little water, and heat gently for some time.

This operation effects the separation of the silicic acid, and the solution of the bases in the form of chlorides. Filter, wash the residue thoroughly, and examine the solution by the common method, beginning at § 188.† To be quite safe, the residuary silicic acid may be digested with ammonia, filtered, and the filtrate tested for silver, by supersaturation with nitric acid.

2. As in silicates, and more particularly in those decomposed by 223

* Nitric acid is preferable to hydrochloric acid in cases where compounds of silver or lead are present.

† Minute traces of titanic acid are occasionally met with in silicates. The titanic acid present passes into the hydrochloric acid solution, if the separation of the silicic acid has been effected on the water-bath, and is subsequently thrown down with the bases precipitable by ammonia (sesquioxide of iron and alumina). Upon igniting the precipitate, and then treating it with concentrated hydrochloric acid, the greater portion of the titanic acid remains undissolved. On filtering it, the washings generally look milky when passing through the filter. It is more closely examined before the blowpipe; compare § 103 (*H. Rose*).

hydrochloric acid, there are often found other acids, as well as metalloids, the following observations and instructions must be attended to, that none of these substances may be overlooked:—

a. SULPHIDES of METALS and CARBONATES are detected in the process of treating with hydrochloric acid.

β. If the separated silicic acid is black, and turns subsequently white upon ignition in the air, this indicates the presence of CARBON or of ORGANIC SUBSTANCES. In presence of the latter, the silicates emit an empyreumatic odor upon being heated in a glass tube.

γ. Test the portion of the hydrochloric acid solution filtered off before evaporating (**222**), for PHOSPHORIC ACID (ARSENIC ACID, which may happen to be present), and SULPHURIC ACID, by means of molybdic acid, and chloride of barium.

δ. BORACIC ACID is best detected by fusing a portion **224**
of the substance in a platinum spoon with carbonate of soda and potassa, boiling the fused mass with water, and examining the solution for boracic acid by the method given in § 145, 6.

ε. With many silicates, boiling with water is sufficient to dissolve the metallic CHLORIDES present, which may then be readily detected in the filtrate by means of solution of nitrate of silver; the safest way, however, is to dissolve the mineral in dilute nitric acid, and test the solution with nitrate of silver.

ζ. Metallic FLUORIDES, which often occur in silicates in greater or smaller proportion, are detected by the methods described § 147.

b. Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.

Heat the finely pulverized mineral with moderately concentrated **225**
pure sulphuric acid (best in a platinum dish), finally drive off the sulphuric acid, boil the residue with hydrochloric acid, dilute, filter, and treat the filtrate as directed § 188; and the residue, which, besides the separated silicic acid, may contain also sulphates of the alkaline earths, &c., according to the directions of § 201. If you wish to examine silicates of this class for acids and salt-radicals, treat a separate portion of the substance according to the directions of § 205.

B. SILICATES WHICH ARE NOT DECOMPOSED BY ACIDS.

§ 205.

As the silicates of this class are most conveniently decomposed by **226**
fusion with carbonate of soda and potassa, the portion so treated cannot, of course, be examined for alkalies. The analytical process is therefore properly divided into two principal parts, viz., a portion of the mineral is examined for the silicic acid and the bases, with the exception of the alkalies, whilst another portion is specially examined for the latter.—Besides these, there are some other experiments required, to obtain information as to the presence or absence of other acids.

1. *Detection of the silicic acid and the bases, with the exception of the alkalies.*

Reduce the mineral to a very fine powder, mix this with 4 **227**
parts of carbonate of soda and potassa, and heat the mixture in a

platinum crucible over a gas or *Berzelius* spirit-lamp, until the mass is in a state of calm fusion. Put the red-hot crucible on a thick, cold iron plate, and let it cool there; this will generally enable you to remove the fused cake from the crucible, in which case break the mass to pieces, and keep a portion for subsequent examination for acids. Put the remainder, or, if the mass still adheres to the crucible, the latter, with its contents, into a porcelain dish, pour water over it, add hydrochloric acid, and heat gently until the mass is dissolved, with the exception of the silicic acid, which separates in flakes. Remove the crucible from the dish, if necessary, evaporate the contents of the latter to dryness, and treat the residue as directed § 204, 1 (**222**).

2. *Detection of the alkalies.*

To effect this, the silicates under examination must be decomposed by means of a substance free from alkalies. Hydrofluoric acid or a metallic fluoride answers this purpose best; but fusion with hydrate of baryta will also accomplish the end in view. **228**

a. DECOMPOSITION BY MEANS OF A METALLIC FLUORIDE.—Mix 1 part of the very finely pulverised mineral with 5 parts of fluoride of barium, or pure, finely pulverized fluoride of calcium, stir the mixture in a platinum crucible with concentrated sulphuric acid to a thickish paste, and heat gently for some time in a place affording a free escape to the vapors; finally heat a little more strongly, until the excess of sulphuric acid is completely expelled. Boil the residue now with water, add chloride of barium cautiously as long as a precipitate continues to form, then baryta-water to alkaline reaction, boil, filter, mix with carbonate of ammonia and some ammonia as long as a precipitate forms, and proceed exactly as directed § 194, 2 (**168**).

b. DECOMPOSITION BY MEANS OF HYDRATE OF BARYTA. Mix **229**
1 part of the very finely pulverized substance with 4 parts of hydrate of baryta, expose the mixture for half an hour in a platinum crucible to the strongest possible heat of a good *Berzelius* or gas-lamp, and treat the fused or agglutinated mass with hydrochloric acid and water until it is dissolved; precipitate the solution with ammonia and carbonate of ammonia, filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, ignite, and test the residue for potassa and soda as directed § 195. If the residue still contains magnesia, this may be readily removed, by adding to the aqueous solution of the residue, a little finely pulverized oxide of mercury, evaporating to dryness, igniting the dry mass, and then treating it with water, which will dissolve the alkalies as chlorides, and leave the magnesia undissolved.

3. *Examination for fluorine, chlorine, boracic acid, phosphoric acid, arsenic acid, and sulphuric acid.*

Use for this purpose the portion of the fused mass reserved in **230**
§ 205, 1 (**227**), or, if necessary, fuse a separate portion of the finely pulverized substance with 4 parts of pure carbonate of soda and potassa until the mass flows calmly; boil the fused mass with water, filter the solution, which contains all the fluorine as fluoride of sodium, all the chlorine as chloride of sodium, all the boracic acid

as borate, all the sulphuric acid as sulphate, all the arsenic acid as arsenate, and at least part of the phosphoric acid as phosphate of soda, and treat the filtrate as follows:—

a. Acidify a small portion of it with nitric acid, and test for chlorine with nitrate of silver.

b. Test another portion for boracic acid as directed § 205, 2, δ (**224**).

c. Test a third portion, after addition of hydrochloric acid, with molybdate of ammonia for phosphoric acid and arsenic acid.

d. To effect the detection of the fluorine, treat the remainder of the filtrate as directed § 147, 7.

C. Silicates which are partially decomposed by Acids.

§ 206.

Most of the native rocks and minerals are mixtures of several **231**
silicates, of which the one is often decomposed by acids, the other not. If such minerals were analyzed by the same method as the absolutely insoluble silicates, the analyst would indeed detect all the elements present, but the analysis would afford no satisfactory insight into the actual composition of the mineral.

It is, therefore, advisable to examine separately those parts of the mineral which show a different deportment with acids. For this purpose digest the very finely pulverized mineral for some time with hydrochloric acid at a very gentle heat, then evaporate to dryness, and expose to a temperature somewhat exceeding 212° F., with stirring, until no more, or very few, hydrochloric acid vapors are evolved; let the residue cool, moisten it when cold with hydrochloric acid, heat gently with water, and filter.

The filtrate contains the bases of the decomposed part of the mixed mineral; examine this as directed § 204. The residue contains, besides the silicic acid separated from these bases by the action of the hydrochloric acid, that part of the mixed mineral which has resisted the action of the acid. Boil this residue with an excess of solution of carbonate of soda, filter hot, and wash, first with hot solution of carbonate of soda, finally with boiling water. Treat the residuary undecomposed part of the mineral, from which the admixed free silicic acid has thus been removed, according to the instructions given in § 205. In cases where it is of no consequence or interest to effect the separation of the silicic acid of the part decomposed by acids, you may omit the laborious treatment with carbonate of soda, and may proceed at once to the decomposition of the residue.

III. Analysis of Natural Waters.

§ 207.

In the examination of natural waters the analytical process is **232**
simplified by the circumstance that we know from experience the elements and compounds which are usually found in them. Now, although a quantitative analysis alone can properly inform us as to the true nature and character of a water, since the differences be-

tween the various waters are principally caused by the different proportions in which the several constituents are respectively present, a qualitative analysis may yet render very good service, especially if the analyst notes with proper care, whether a reagent produces a faint or a distinctly marked turbidity, a slight or a copious precipitate, since these circumstances will enable him to make an approximate estimation of the relative proportions in which the several constituents are present.

I separate here the analysis of the common fresh waters (spring-water, well-water, brook-water, river-water, &c.) from that of the mineral waters, in which we may also include sea-water; for, although no well-defined limit can be drawn between the two classes, still the analytical examination of the former is necessarily far more simple than that of the latter, as the number of substances to be looked for is much more limited than in the case of mineral waters.

A. Analysis of Fresh Waters (Spring-water, Well-water, Brook-water, River-water, &c.).

§ 208.

We know from experience that the substances to be had regard 233
to in the analysis of such waters are the following :—

a. Bases : Potassa, soda, ammonia, lime, magnesia, protoxide of iron.

b. Acids, &c. : Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, chlorine.

c. Organic matters.

d. Mechanically suspended substances : Clay, &c.

The fresh waters contain indeed also other constituents besides those enumerated here, as may be inferred from the origin and formation of springs, &c., and as has, moreover, been fully established by the results of analytical investigations;* but the quantity of such constituents is so trifling that they escape detection, unless hundreds of pounds of the water are subjected to the analytical process. I omit, therefore, here the mode of their detection, and refer to § 209.

1. Boil the carefully collected water in a glass flask or retort 234
to one half. This generally produces a precipitate. Pass the fluid through a perfectly clean filter (free from iron and lime), wash the precipitate well, after having removed the filtrate, and then examine both as follows :—

a. Examination of the precipitate.

The precipitate contains those constituents of the water 235
which were only kept in solution through the agency of free

* *Chatin* ("Journ. de Pharm. et de Chim.," 3 Sér. t. xxvii. p. 418) found iodine in all fresh-water plants, but not in land plants, a proof that the water of rivers, brooks, ponds, &c., contains traces, even though extremely minute, of metallic iodides. According to *Marchand* ("Compt. Rend.," t. xxxi. p. 495), all natural waters contain iodine, bromine, and lithia. Van Ankum has demonstrated the presence of iodine in almost all the potable waters of Holland. And it may be affirmed with the same certainty that all, or at all events most, natural waters contain compounds of strontia, fluorine, &c.

carbonic acid, or, as the case may be, in the form of bicarbonates, viz., carbonate of lime, carbonate of magnesia, hydrated sesquioxide of iron (which was in solution as bicarbonate of protoxide of iron, and precipitates upon boiling as sesquioxide, and if phosphoric acid is present, also in combination with that acid), phosphate of lime; and besides, silicic acid, and sometimes also sulphate of lime, if that substance is present in large proportion; and clay which was mechanically suspended in the water.

Dissolve the precipitate on the filter in the least possible quantity of dilute hydrochloric acid (effervescence indicates the presence of CARBONIC ACID), and mix separate portions of the solution :—

a. With sulphocyanide of potassium : red coloration indicates the presence of IRON ;

β. With ammonia; warm, filter, if necessary, mix the 236
filtrate with oxalate of ammonia, and let the mixture stand for some time in a warm place. The formation of a white precipitate indicates the presence of LIME—in the form of carbonate, or also in that of sulphate if sulphuric acid is detected in *γ*. Filter, mix the filtrate again with ammonia, add some phosphate of soda, stir with a glass rod, and let the mixture stand for twelve hours. The formation of a white, crystalline precipitate, which is often visible only on the sides of the vessel when the fluid is poured out, indicates the presence of MAGNESIA (carbonate of);

γ. With chloride of barium, and let the mixture stand for twelve hours in a warm place. The formation of a precipitate—which, when very inconsiderable, is best seen if the supernatant clear fluid is cautiously decanted, and the small quantity remaining shaken about in the glass—indicates the presence of SULPHURIC ACID.

δ. Add some of the fluid to a solution of molybdate of 237
ammonia, acidified with hydrochloric acid, and boil. The appearance of a yellow color, or the formation of a yellow precipitate, indicates the presence of PHOSPHORIC ACID.*

b. Examination of the filtrate.

a. Mix a portion of the filtrate with a little hydrochloric 238
acid and chloride of barium. The formation of a white precipitate, which makes its appearance at once or perhaps only after standing some time, indicates SULPHURIC ACID.

β. Mix another portion with nitric acid, and add nitrate of silver. A white precipitate or a white turbidity, indicates the presence of CHLORINE.

γ. Test a portion of the filtrate for PHOSPHORIC ACID as in *a*, *δ* (237).

δ. Evaporate another and larger portion of the filtrate until 239

* In default of molybdate of ammonia, evaporate the remainder of the hydrochloric acid solution of the precipitate to dryness, redissolve the residue in a little hydrochloric acid and water, filter the solution, and mix the filtrate with carbonate of soda until it is nearly neutralized, then with acetate of soda and a very small quantity of sesquichloride of iron. The formation of a white precipitate, which generally becomes visible only after long standing, indicates the presence of PHOSPHORIC ACID.

highly concentrated, and test the reaction of the fluid. If it is alkaline, and a drop of the concentrated clear solution effervesces when mixed on a watch-glass with a drop of acid, a CARBONATE of an alkali is present. Should this be the case, evaporate the fluid to perfect dryness, boil the residue with spirit of wine, filter, evaporate the alcoholic solution to dryness, dissolve the residue in a little water, and test the solution for NITRIC ACID as directed § 159, 5, or by the method given in § 159, 8, which is still more delicate.

ε. Mix the remainder of the filtrate with some chloride of ammonium, add ammonia and oxalate of ammonia, and let the mixture stand for a considerable time. The formation of a precipitate indicates the presence of LIME. Filter, and test,—

aa. A small portion with ammonia and phosphate of soda for MAGNESIA.

bb. Evaporate the remainder to dryness, heat the residue to redness, remove the magnesia, which may be present (§ 194), and test for POTASSA and SODA, according to the directions of § 195.

2. Acidify a tolerably large portion of the filtered water with pure hydrochloric acid, and evaporate nearly to dryness; divide the residue into 2 parts, and,— **240**

a. Test the one part with hydrate of lime for AMMONIA (compare § 196).

b. Evaporate the other part to dryness, moisten with hydrochloric acid, add water, warm, and filter, if a residue remains. The residue may consist of SILICIC ACID, and of CLAY which has been mechanically suspended in the water; these two substances may be separated from each other by boiling with solution of carbonate of soda. The precipitate is often dark-colored from the presence of organic substances; but it becomes perfectly white upon ignition.

3. Mix another portion of the water, fresh taken from the well, &c., with lime-water. If a precipitate is thereby produced, FREE CARBONIC ACID or BICARBONATES are present. If the former is present (free carbonic acid), no permanent precipitate is obtained when a larger portion of the water is mixed with only a small amount of lime-water, since in that case soluble bicarbonate of lime is formed. **241**

4. To detect the presence of ORGANIC MATTERS, evaporate a portion of the water to dryness, and gently ignite the residue: blackening of the mass denotes the presence of organic substances. If this experiment is to give conclusive results, the evaporation of the water, as well as the ignition of the residue, must be conducted in a glass flask or a retort. **242**

5. If you wish to examine the MATTERS MECHANICALLY SUSPENDED in a water (in muddy brook or river-water, for instance), fill a large glass bottle with the water, cork securely, and let it stand at rest for several days, until the suspended matter has subsided; remove now the clear supernatant fluid with the aid of a syphon, filter the remainder, and examine the sediment remaining on the filter. As this sediment may consist of the finest dust of various minerals, treat it first with hydrochloric acid, and examine the part insoluble **243**

in that menstruum in the manner directed § 203 (Analysis of Silicates).

B. Analysis of Mineral Waters.

§ 209.

The analysis of mineral waters embraces a larger number of constituents than that of fresh water. The following are the principal of the additional elements to be looked for :— 244

LITHIA, BARYTA, STRONTIA, ALUMINA, PROTOXIDE OF MANGANESE, BORACIC ACID, BROMINE, IODINE, FLUORINE, HYDROSULPHURIC ACID, CRENIC ACID and APOCRENIC ACID.

The analyst has, moreover, to examine the muddy ochreous or hard sinter-deposits of the spring for ARSENIOUS ACID, ARSENIC ACID, OXIDE OF COPPER, OXIDE OF LEAD, and the oxides of other heavy metals. The greatest care is required in this examination, to ascertain whether these oxides come really from the water, and do not proceed from metal pipes, stopcocks, &c.* The absolute purity of the reagents employed in these delicate investigations must also be ascertained with the greatest care.

1. Examination of the Water.

a. Operations at the Spring.

§ 210.

1. Filter the water at the spring, if not perfectly clear, through Swedish filter paper, and collect the filtrate in large bottles with glass stoppers. The sediment remaining on the filter, which contains, besides the flocculent matter suspended in the water, also those constituents which separate at once upon coming in contact with the air (hydrate of sesquioxide of iron, and compounds of sesquioxide of iron with phosphoric acid, silicic acid, arsenic acid), is taken to the laboratory, to be examined afterwards according to the directions of § 212. 245

2. The presence of FREE CARBONIC ACID is usually sufficiently visible to the eye. However, to convince yourself by positive reactions, test the water with fresh-prepared solution of litmus, and with lime-water. If carbonic acid is present, the former acquires a wine-red color ; the latter produces turbidity, which must disappear again upon addition of the mineral water in excess. 246

3. Free HYDROSULPHURIC ACID is most readily detected by the smell. For this purpose half fill a bottle with the mineral water, cover with the hand, shake, take off the hand, and smell the bottle. In this way distinct traces of hydrosulphuric acid are often found, which would escape detection by reagents. However, if you wish to have some visible reactions, fill a large white bottle with the water, add a few drops of solution of acetate of lead in solution of soda, place the bottle on a white surface, and look in at the top, to 247

* Compare "Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau," von Professor Dr. *Fresenius ;* I. Der Kochbrunnen zu Wiesbaden ; II. Die Mineralquellen zu Ems ; III. die Quellen zu Schlangenbad ; IV. die Quellen zu Langenschwalbach ; published at Wiesbaden, by *Kriedel* und *Niedner*. 1850–1855.

see whether the water acquires a brownish color or deposits a blackish precipitate ;—or half fill a large bottle with the water, and close with a cork to which is attached a small slip of paper, previously steeped in solution of acetate of lead and then moistened with a little solution of carbonate of ammonia; shake the bottle gently from time to time, and observe whether the paper slip acquires a brownish tint in the course of a few hours. If the addition of the solution of acetate of lead to the water has imparted a brown color to the fluid or produced a precipitate in it, whilst the reaction with the paper slip gives no result, this indicates that the water contains an alkaline sulphide, but no free hydrosulphuric acid.

4. Mix a wineglass-full of the water with some tannic acid, **248** another wineglass-full with some gallic acid. If the former imparts a blue violet, the latter a red violet color to the water, PROTOXIDE OF IRON is present. Instead of the two acids, you may employ infusion of galls, which contains them both.

b. Operations in the Laboratory.

§ 211.

As it is always desirable to obtain even in the qualitative examination some information as to the quantitative composition of a mineral water, *i. e.* as to the proportions in which the several constituents are contained in it, it is advisable to analyze a comparatively small portion for the principal constituents, and to ascertain, as far as may be practicable, the relative proportions in which these constituents exist, and thus to determine the character of the water; and then to examine a very large amount of the water for those elements which are present only in minute quantities. For this purpose proceed as follows :—

1. Examination for those constituents of the water which **249** are present in larger quantities. — Boil about 3lbs. of the clear water, or of the filtrate, brought from the spring, in a glass flask for 1 hour, taking care, however, to add from time to time some distilled water, that the quantity of liquid may remain undiminished, and thus the separation of any but *those* salts be prevented which owe their solution to the presence and agency of carbonic acid. Filter after an hour's ebullition, and examine the precipitate and the filtrate as directed § 208.

2. Examination for those fixed constituents of the water **250** which are present in minute quantities only.—Evaporate a large quantity (at least 20 lbs.) of the water in a silver or porcelain dish to dryness; conduct this operation with the most scrupulous cleanliness in a place as free as possible from dust. If the water contains no carbonate of an alkali, add pure carbonate of potassa to slight predominance. The process of evaporation may be conducted in the first place over a gas-lamp, but ultimately the sand-bath must be employed. Heat the dry mass to very faint redness; if in a silver dish, you may at once proceed to ignite it; but if you have it in a porcelain dish, first transfer it to a silver or platinum vessel before proceeding to ignition. If the mass

turns black in this process, ORGANIC MATTERS may be assumed to be present.*

Mix the residue thoroughly, that it may have the same composition throughout, and then divide it into 3 portions, one (*c*) amounting to about one-half, and each of the other two (*a* and *b*) to one-fourth.

a. EXAMINATION FOR IRON, PHOSPHORIC ACID (ARSENIC ACID).

Warm the portion *a* with some water, add perfectly pure hydrochloric acid in moderate excess, digest for some time at a temperature near the boiling point, filter through paper washed with hydrochloric acid and water, and test. 251

α. A sample for IRON, by means of sulphocyanide of potassium.

β. Treat the remainder with hydrosulphuric acid, let the fluid saturated with that acid stand for twenty-four hours, filter from the separated sulphur, concentrate the filtrate by boiling, and test it with molybdate of ammonia for PHOSPHORIC ACID.

γ. If the sulphur deposited in *β* is not perfectly white, treat it as directed § 212, 1, *a*, *α* (**263**), in order to detect the arsenic, copper, &c., which may be present.

b. EXAMINATION FOR FLUORINE.

Heat the portion *b* with water, add chloride of calcium as long as a precipitate continues to form, let deposit; filter the fluid from the precipitate, which consists chiefly of carbonate of lime and carbonate of magnesia. After having washed and dried the precipitate, ignite, then pour water over it in a small dish, add acetic acid in slight excess, evaporate on the water-bath to dryness, heat until all smell of acetic acid has disappeared, add water, heat again, filter the solution of the acetates of the alkaline earths, wash, dry or ignite the residue, and test it for FLUORINE as directed § 147, 5. 252

c. EXAMINATION FOR THE REMAINING CONSTITUENTS PRESENT IN MINUTE QUANTITIES. 253

Boil the portion *c* repeatedly with water, filter, and wash the undissolved residue with boiling water. You have now a residue (*α*), and a solution (*β*).

α. The *residue* consists chiefly of carbonate of lime, carbonate of magnesia, and—in the case of chalybeate springs—hydrate of sesquioxide of iron. But it may contain also minute quantities of BARYTA, STRONTIA, ALUMINA, and PROTOXIDE OF MANGANESE, and must accordingly be examined for these substances. 254

Put the residue in a platinum or porcelain dish, pour water over it, add hydrochloric acid to slightly acid reaction, then 4 or 5 drops of dilute sulphuric acid, evaporate to dryness, moisten with hydrochloric acid, then add water,

* This inference is, however, correct only if the water has been effectually protected from dust during the process of evaporation; if this has not been the case, and you yet wish to ascertain beyond doubt whether organic matters are present, evaporate a separate portion of the water in a retort. If you find organic matter, and wish to know whether it consists of crenic acid or of apocrenic acid, treat a portion of the residue as directed § 212, 3.

warm gently, filter, and wash the residue which is left undissolved.

aa. EXAMINATION OF THE RESIDUE INSOLUBLE IN HYDROCHLORIC ACID FOR BARYTA AND STRONTIA. 255

This residue will generally consist of silicic acid; but it may contain also sulphates of the alkaline earths and carbon. If there is much silicic acid present, remove this in the first place, as far as practicable, by boiling with dilute solution of soda; filter, wash the residue, if any has been left, dry, incinerate the filter in a platinum crucible, add some carbonate of soda and potassa and, in presence of carbon, some nitrate of potassa, and ignite for some time. If the residue contains but little silicic acid, the treatment with solution of soda may be omitted, and the fusion with carbonate of potassa and soda, &c., at once proceeded with. Boil the fused mass with water, filter, wash thoroughly, dissolve the residue (which must have been left, if sulphates of the alkaline earths were present) on the filter in the least possible quantity of dilute hydrochloric acid, add an equal volume of spirit of wine, then some pure hydrofluosilicic acid, and let the mixture stand 12 hours. If in the course or at the end of the 12 hours a precipitate makes its appearance, this denotes the presence of BARYTA. Filter, and warm the filtrate in a platinum dish, adding from time to time some water, until the spirit of wine is quite driven off. Mix the fluid now with saturated solution of sulphate of lime. If this produces a precipitate, whether after some time or after several hours' standing, this precipitate consists of sulphate of STRONTIA. To make quite sure, examine it before the blowpipe (see § 95, 7).

bb. EXAMINATION OF THE HYDROCHLORIC ACID SOLUTION FOR PROTOXIDE OF MANGANESE AND ALUMINA. 256

Mix the solution in a flask with some pure chloride of ammonium, add ammonia until the fluid is just turning alkaline, then some yellow sulphide of ammonium, close the flask, and let it stand for 12 hours in a moderately warm place. If a precipitate has formed at the end of that time, filter, dissolve the precipitate in hydrochloric acid, boil, add solution of potassa (§ 30, *c*) in excess, boil again, filter, and test the filtrate for ALUMINA;* the residue with carbonate of soda before the blowpipe for MANGANESE.

β. The *alkaline solution* contains the salts of the alkalies, 257
and usually also magnesia and traces of lime. You have to examine it now for NITRIC ACID,† BORACIC ACID, IODINE,

* You are not justified in regarding this substance as an ingredient of the water, except in cases where the process of evaporation has been conducted in a platinum or silver dish, but not in a porcelain dish.

† The nitric acid originally present may have been destroyed by the ignition of the residue in § 211, 2 (**250**), if the latter contained organic matter. If you have reason to fear that such has been the case, and you have not already found nitric acid in § 211, 1, examine a larger portion of non-ignited residue for that acid, according to the directions of § 211, 2, *c*, *β*, *aa* (**258**).

BROMINE, and LITHIA. Evaporate the fluid until *highly* concentrated, let it cool, and place the dish in a slanting position, that the small quantity of liquid may separate from the saline mass; pour a few drops of the concentrated solution in a watch-glass, acidify very slightly with hydrochloric acid, and test with turmeric paper for BORACIC ACID. Pour back into the dish the remainder of the liquid, of which you have just tested a few drops, evaporate, with stirring, to perfect dryness, and divide the residuary powder into 2 portions, one (*aa*) of two-thirds, the other (*bb*) of one-third.

aa. EXAMINE THE LARGER PORTION FOR NITRIC ACID, IODINE, AND BROMINE. 258

Put the powder into a flask, pour pure spirit of wine of 90 per cent. over it, boil on the water bath, and filter hot; repeat the same operation a second and a third time. Mix the alcoholic extract with a few drops of solution of potassa, distil the spirit of wine off to within a small quantity, and let cool. If minute crystals separate, these may consist of nitrate of potassa; pour off the fluid, wash the crystals with some spirit of wine, dissolve them in a very little water, and test the solution for nitric acid, best by means of brucia (§ 159, 8). Evaporate the alcoholic solution now to dryness. If you have not yet found nitric acid, dissolve a small portion of the residue in a very little water, and examine the solution for that acid. Treat the remainder of the residue or, if it has been unnecessary to search for nitric acid, the entire residue, three times with warm alcohol, filter, evaporate the filtrate to dryness, dissolve the residue in a very little water, add some starch-paste, acidify slightly with sulphuric acid, and test for iodine by adding some nitrite of potassa in solution, or a drop of solution of hyponitric acid in sulphuric acid. After having carefully observed the reactions, test the same fluid for bromine with ether and chlorine water in the manner described in § 157.

bb. EXAMINE THE SMALLER PORTION FOR LITHIA.

Warm the smaller portion of the residue, which, 259
if lithia is present, must contain that alkali as carbonate or phosphate, with water, add hydrochloric acid to distinctly acid reaction, evaporate *nearly* to dryness, and then mix with pure spirit of wine of 90 per cent., which will separate the greater portion of the chloride of sodium, and give all the lithia in the alcoholic solution. Drive off the alcohol by evaporation, dissolve the residue in water mixed with a few drops of hydrochloric acid, add a little sesquichloride of iron, then ammonia in *slight* excess, and a small quantity of oxalate of ammonia, and let the mixture stand for some time; then filter off the fluid, which is now entirely free from phosphoric acid and lime; evaporate the filtrate to dryness, and gently ignite the residue, until the salts of ammonia are expelled;

treat the residue with some chlorine water (to remove the iodine and bromine) and a few drops of hydrochloric acid, and evaporate to dryness; add a little water and (to remove the magnesia) some finely divided oxide of mercury, evaporate to dryness, and gently ignite the residue, until the chloride of mercury is completely driven off; treat the residue now with a mixture of absolute alcohol and anhydrous ether, filter the solution obtained, concentrate the filtrate by evaporation, and set fire to the alcohol. If it burns with a carmine flame, LITHIA is present. By way of confirmation, convert the lithia found into phosphate of LITHIA.*

3. If you have not yet clearly detected ammonia in 1 (249), add 260
to a large quantity of the water hydrochloric acid to acid reaction, and concentrate the fluid considerably by boiling in a retort. Add now, through the tubular neck of the retort, an excess of milk of lime, made with recently calcined hydrate of lime, boil, and conduct the vapor into a flask containing very dilute hydrochloric acid, which is kept cool by surrounding it with ice or with very cold water; evaporate the contents almost to dryness, and then test for ammonia with hydrate of lime or with bichloride of platinum.

2. Examination of the Sinter-Deposit.

§ 212.

1. Free the ochreous or sinter-deposit from impurities, by picking, 261
sifting, elutriation, &c., and from the soluble salts adhering to it, by washing with water; digest a large quantity (about 200 grammes) of the residue with water and hydrochloric acid (effervescence: CARBONIC ACID) until the soluble part is completely dissolved; dilute, cool, filter, and wash the residue.

a. Examination of the filtrate.

α. Saturate the larger portion of the filtrate nearly with 262
carbonate of soda, add a few drops of dilute sulphuric acid, and let the mixture stand for 24 hours at a gentle heat. If a precipitate is found to have formed after this time, filter, wash the precipitate, pour hydrosulphuric acid over it, that you may not overlook the possible presence of sulphate of lead, and test for BARYTA and STRONTIA as directed § 211, 2, *c*, *a*, *aa* (255). Boil the fluid filtered from this precipitate with sulphite of soda—if necessary, with addition of some hydrochloric acid, as the fluid must always remain acid—to reduce the sesquioxide of iron to protoxide, and the arsenic acid, which may be present, to arsenious acid; heat finally, until all sulphurous acid is expelled, and conduct for some hours a slow stream of washed hydrosulphuric acid gas into the fluid; let the latter now stand in a moderately warm place, until the smell of hydrosulphuric acid has become quite faint. If a precipitate has formed, 263

* The precipitate designated in § 92 as phosphate of soda and lithia, is $3\ LiO,\ PO_5$ (*Mayer*, "Annal. d. Chem. u. Pharm.," 98, 193).

filter, wash, and digest with dilute solution of soda and some sulphide of sodium; filter, and mix the filtrate with hydrochloric acid to acid reaction. If a precipitate is produced, test,—

a. A portion of it for ARSENIC, with cyanide of potassium and carbonate of soda in a stream of carbonic acid.

b. Treat the remainder as directed § 190, that traces of ANTIMONY and TIN, which may be present, may not be overlooked.

If a residue has been left upon treating the precipitate **264**
produced by hydrosulphuric acid with solution of soda and sulphide of sodium, boil it, together with the filter, with a very little dilute nitric acid, filter, wash, and examine the contents of the filter, as directed in § 212, *a*, *a* (**262**), for sulphate of lead, sulphate of baryta, and sulphate of strontia (the two latter salts are more soluble in solution of sesquichloride of iron than in solution of protochloride of iron. Mix the filtrate (the nitric acid solution) with some pure sulphuric acid, evaporate on the water-bath to dryness, and treat the residue with water. If this leaves an undissolved residue, the latter consists of sulphate of LEAD. To make quite sure, filter, wash the residue, treat it with hydrosulphuric acid water, and observe whether that reagent imparts a black color to it. Test the fluid filtered from the sulphate of lead which may have separated, *a* with ammonia, *b* with ferrocyanide of potassium, for COPPER.

Of the fluid filtered from the precipitate produced by **265**
hydrosulphuric acid, examine in the first place, after having expelled the hydrosulphuric acid by boiling, a portion with molybdate of ammonia for PHOSPHORIC ACID; mix the remainder in a flask with chloride of ammonium, ammonia, and yellowish sulphide of ammonium, close the flask, and let it stand in a moderately warm place until the fluid above the precipitate looks no longer greenish, but yellow; filter, and wash the precipitate with water to which some sulphide of ammonium has been added. Dissolve the washed precipitate in hydrochloric acid, separate the SILICIC ACID by evaporation, moisten the residue with hydrochloric acid, add water, warm, and test the solution for ALUMINA, IRON, MANGANESE, and ZINC, according to the directions of § 192, 1. Examine now the fluid filtered from the precipitate produced by sulphide of ammonium, for LIME and MAGNESIA in the usual way.

β. Mix a portion of the hydrochloric acid solution with chloride of barium, and let the mixture stand 12 hours in a warm place. The formation of a white precipitate indicates the presence of SULPHURIC ACID.

b. Examination of the residue.

This consists usually of silicic acid, clay, and organic mat- **266**
ters, but it may also contain sulphate of baryta and sulphate of strontia. Boil in the first place with solution of soda or potassa, to dissolve the SILICIC ACID; then fuse the residue

with carbonate of soda and potassa, and a little nitrate of potassa. Boil the mass, wash the residue, and then dissolve it in some hydrochloric acid; boil the solution, add ammonia, filter the fluid from the ALUMINA, &c., which may precipitate, evaporate the filtrate to dryness, gently ignite the residue, redissolve it in very little water, with addition of a drop of hydrochloric acid, and test for BARYTA and STRONTIA as directed § 211, 2, *c*, *a*, *aa* (**255**).

2. As regards the examination for FLUORINE, the best way is to take for this purpose a separate portion of the ochreous or sinter-deposit. Ignite (which operation will also reveal the presence of organic matters), stir with water, add acetic acid to acid reaction, evaporate until the acetic acid is completely expelled, and proceed as described in § 211, 2, *b* (**252**). **267**

3. Boil the ochreous or sinter-deposit for a considerable time with concentrated solution of potassa or soda, and filter. **268**

a. Acidify a portion of the filtrate with acetic acid, add ammonia, let the mixture stand 12 hours, and then filter the fluid from the precipitate of alumina and hydrated silicic acid, which usually forms; again add acetic acid to acid reaction, and then a solution of neutral acetate of copper. If a brownish precipitate is formed, this consists of APOCRENATE of copper. Mix the fluid filtered from the precipitate with carbonate of ammonia, until the green color has changed to blue, and warm. If a bluish-green precipitate is produced, this consists of CRENATE of copper.

b. If you have detected arsenic, use the remainder of the alkaline fluid to ascertain whether the arsenic existed in the sinter as arsenious acid or as arsenic acid. Compare § 133, 6.

IV. ANALYSIS OF SOILS.

§ 213.

Soils must necessarily contain all the constituents which are found in the plants growing upon them, with the exception of those supplied by the atmosphere and the rain. When we find, therefore, a plant the constituent elements of which are known, growing in a certain soil, the mere fact of its growing there gives us some insight into the composition of that soil, and may accordingly save us, to some extent, the trouble of a qualitative analysis.

Viewed in this light, it would appear quite superfluous to make a qualitative analysis of soils still capable of producing plants; for it is well known that the ashes of plants contain almost invariably the same constituents, and the differences between them are caused principally by differences in the relative proportions in which the several constituents are present. But if, in the qualitative analysis of a soil, regard is had also—in so far as may be done by a simple estimation—to the quantities and proportions of the several constituent ingredients, and to the state and condition in which they are found to be present in the soil, an analysis of the kind, if combined with an examination of the physical properties of the soil,

and a mechanical separation of its component parts,* may give most useful results, enabling the analyst to judge sufficiently of the condition of the soil, to supersede the necessity of a *quantitative* analysis, which would require much time, and is a far more difficult task.

As plants can only absorb substances in a state of solution, it is a matter of especial importance, in the qualitative analysis of a soil, to know which are the constituents that are soluble in water; which those that require an acid for their solution (in nature principally carbonic acid); and, finally, which those that are neither soluble in water nor in acids, and are not, accordingly, in a position for the time being to afford nutriment to the plant. With regard to the insoluble substances, another interesting question to answer is, whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether resist the action of disintegrating agencies; and also what are the products which they yield upon their disintegration.†

In the analysis of soils, the constituents soluble in water, those soluble in acids, and the insoluble constituents must be examined separately. The examination of the organic portion also demands a separate process.

The analysis is therefore properly divided into the following four parts:

1. *Preparation and Examination of the Aqueous Extract.*

§ 214.

About two pounds (1000 grammes) of the air-dried soil are used for the preparation of the aqueous extract. To prepare this extract quite clear is a matter of some difficulty; in following the usual course, viz., digesting or boiling the earth with water, and then filtering, the fine particles of clay are speedily found to impede the operation, by choking up the pores of the filter; they also almost invariably render the filtrate turbid, at least the portion which passes through first. I have found the following method the most practical.‡ Close the neck of several middle-sized funnels with small filters of coarse blotting paper, moisten the paper, press it close to the sides of the funnels, and then introduce the air-dried soil, in small lumps ranging from the size of a pea to that of a walnut, but not pulverized or even crushed; fill the funnels with the soil to the extent of about two-thirds. Pour distilled water into them, in sufficient quantity to cover the soil; if the first portion of the filtrate is turbid, pour it back on the filter. Let the operation proceed quietly. When the first quantity of the fluid has passed, fill the 269

* With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties and chemical condition, compare *Fr. Schulze's* paper "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile."—Journal f. prakt. Chemie, Vol. 47, p. 241.

† For more ample information on this subject I refer the reader to *Fresenius*' "Chemie für Landwirthe, Forstmänner und Cameralisten;" published at Brunswick, by *F. Vieweg and Son*, 1847, p. 485.

‡ Recommended by *Fr. Schulze* "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile."—Journ. f. prakt. Chemie, Vol. 47, p. 241.

funnels a second, and after this a third time. Collect the several filtrates in one vessel. Treat the contents of one of the funnels repeatedly with hot water, in order to remove the soluble matter as far as practicable, the lixiviated soil being required for the preparation of the acid extract.

a. Concentrate two-thirds of the aqueous solution by cautiously evaporating in a porcelain dish, filter off a portion, and test its reaction; put aside a portion of the filtrate for the subsequent examination for organic matters, according to the directions of 4. Warm the remainder, and add nitric acid. Evolution of gas indicates the presence of an ALKALINE CARBONATE. Then test with nitrate of silver for CHLORINE. *b.* Transfer the remainder of the concentrated fluid, together with the precipitate which usually forms in the process of concentration, to a small porcelain, or, which is preferable, a small platinum dish, evaporate to dryness, and cautiously heat the brownish residue over the lamp until complete destruction of the organic matter is effected. In presence of NITRATES this operation is attended with deflagration, which is more or less violent according to the greater or smaller proportion in which these salts are present. *c.* Test a small portion of the gently ignited residue with carbonate of soda before the blowpipe for MANGANESE. *d.* Warm the remainder with water, add some hydrochloric acid (effervescence indicates the presence of CARBONIC ACID), evaporate to dryness, heat a little more strongly, to effect the complete separation of the silicic acid, moisten with hydrochloric acid, add water, warm, and filter. The washed residue generally contains some carbon, and also a little clay—if the aqueous extract was not perfectly clear—and lastly SILICIC ACID. To detect the latter, make a hole in the point of the filter, rinse the residue through, boil with solution of carbonate of soda, filter, saturate with hydrochloric acid, evaporate to dryness, and treat the residue with water, which will leave the silicic acid undissolved. **270**

e. Test a small portion of the hydrochloric acid solution **271** with chloride of barium for SULPHURIC ACID; another portion with molybdate of ammonia for PHOSPHORIC ACID; a third portion with sulphocyanide of potassium for SESQUIOXIDE OF IRON. Add to the remainder a few drops of sesquichloride of iron (to remove the phosphoric acid), then ammonia cautiously until the fluid is slightly alkaline, warm a little, filter, throw down the LIME from the filtrate by means of oxalate of ammonia, and proceed for the detection of MAGNESIA, POTASSA, and SODA, in the usual way, strictly according to the directions of § 194.

f. Alumina is not likely to be found in the aqueous extract. **272** (*Fr. Schulze* never found any). However, if you wish to test for it, boil the ammonia precipitate obtained in *e* **(271)** with pure solution of soda or potassa, filter, and test the filtrate with chloride of ammonium.

g. If you have detected iron, test a portion of the remaining **273** third of the aqueous extract with ferricyanide of potassium, another with sulphocyanide of potassium, both after previous

addition of some hydrochloric acid: this will indicate the degree of oxidation in which the iron is present. Mix the remainder of the aqueous extract with a little sulphuric acid, evaporate on the water-bath nearly to dryness, and test the residue for AMMONIA, by adding hydrate of lime.

2. *Preparation and Examination of the Acid Extract.*

§ 215.

1. Heat about 50 grammes of the soil from which the part soluble in water—both cold and hot—has been removed as far as practicable* (see § 214), with moderately strong hydrochloric acid (effervescence indicates CARBONIC ACID) for several hours on the water-bath, filter, and make the following experiments with the filtrate, which, owing to the presence of sesquichloride of iron, has in most cases a yellow color:— **274**

Test a small portion of it with sulphocyanide of potassium for SESQUIOXIDE OF IRON, another with ferrocyanide of potassium for PROTOXIDE OF IRON. **275**

2. Test a small portion with chloride of barium for SULPHURIC ACID, another with molybdate of ammonia for PHOSPHORIC ACID.

3. Mix a larger portion of the filtrate with ammonia to neutralize the free acid, then with yellowish sulphide of ammonium; and let the mixture stand in a warm place until the fluid looks yellow; then filter, and test the filtrate in the usual way for LIME, MAGNESIA, POTASSA, AND SODA. **276**

4. Dissolve the precipitate obtained in 3 (**276**), in hydrochloric acid, evaporate the solution to dryness, moisten the residue with hydrochloric acid, add water, warm, filter, and examine the filtrate according to the directions of § 192, 2 (**150**), for IRON, MANGANESE, ALUMINA, and, if necessary, also for lime and magnesia, which may have been thrown down by the sulphide of ammonium, in combination with phosphoric acid. **277**

5. The separated SILICIC ACID obtained in 4 is usually colored by organic matter. It must, therefore, be ignited to obtain it pure.

6. If it is a matter of interest to ascertain whether the hydrochloric acid extract contains ARSENIC ACID, OXIDE OF COPPER, &c., treat the remainder of the solution first with sulphite of soda, then with hydrosulphuric acid, as directed in § 223, 1, and 2. **278**

7. Should you wish to look for FLUORINE, ignite a fresh portion of the earth, and then proceed according to the directions of § 205. 3 (**230**).

3. *Examination of the Inorganic Constituents insoluble in Water and Acids.*

§ 216.

The operation of heating the lixiviated soil with hydrochloric acid (§ 215 [**274**]) leaves still the greater portion of it undissolved. If you wish to subject this undissolved residue to a chemical exami- **279**

* Complete lixiviation is generally impracticable.

nation, wash, dry, and sift, to separate the large and small stones from the clay and sand; moreover, separate the two latter from each other by elutriation. Subject the several portions to the analytical process given for the silicates (§ 203).

4. *Examination of the Organic Constituents of the Soil.**

§ 217.

The organic constituents of the soil, which exercise so great an influence upon its fertility, both by their physical and chemical action, are partly portions of plants in which the structure may still be recognised (fragments of straw, roots, seeds of weeds, &c.), partly products of vegetable decomposition, which are usually called by the general name of HUMUS, but differ in their constituent elements and properties, according to whether they result from the decay of the nitrogenous or non-nitrogenous parts of plants—whether alkalies or alkaline earths have or have not had a share in their formation—whether they are in the incipient or in a more advanced stage of decomposition. To separate these several component parts of humus would be an exceedingly difficult task, which, moreover, would hardly repay the trouble; the following operations are amply sufficient to answer all the purposes of a qualitative analysis of the organic constituents of a soil.

a. Examination of the Organic Substances soluble in Water.

Evaporate the portion of the filtrate of 214, *a* (**270**), which has 280
been put aside for the purpose of examining the organic constituents, on the water-bath to perfect dryness, and treat the residue with water. The ulmic, humic, and geic acids, which were in the solution in combination with bases, remain undissolved, whilst crenic acid and apocrenic acid are dissolved in combination with ammonia; for the manner of detecting the latter acids, see § 212, 3 (**268**).

b. Treatment with an Alkaline Carbonate.

Dry a portion of the lixiviated soil, and sift to separate the 281
fragments of straw, roots, &c., together with the small stones, from the finer parts; digest the latter for several hours, at a temperature of 176°—194° F., with solution of carbonate of soda, and filter. Mix the filtrate with hydrochloric acid to acid reaction. If brown flakes separate, these proceed from ulmic acid, humic acid, or geic acid. The larger the quantity of ulmic acid present the lighter, the larger that of humic acid or geic acid, the darker the brown color of the flakes.

c. Treatment with Caustic Alkali.

Wash the soil boiled with solution of carbonate of soda (*b*) with 282
water, boil several hours with solution of potassa, replacing the water

* Compare *Fresenius'* "Chemie für Landwirthe, Forstmänner und Cameralisten;" published at Brunswick, by *F. Vieweg and Son*, 1847, §§ 282—285.

in proportion as it evaporates, dilute, filter, and wash. Treat the brown fluid as in *b*. The ulmic and humic acids which separate now, are new products resulting from the action of boiling solution of potassa upon the ulmine and humine originally present.

V. Detection of Inorganic Substances in Presence of Organic Substances.

§ 218.

The impediments which the presence of coloring, slimy, and other organic substances throw in the way of the detection of inorganic bodies, and that the latter can often be effected only after the total destruction of the organic admixture, will be readily conceived, if we reflect that in dark colored fluids changes of color or the formation of precipitates escape the eye, that slimy fluids cannot be filtered, &c. Now, as these difficulties are very often met with in the analysis of medicinal substances, and more especially in the detection of inorganic poisons in articles of food or in the contents of the stomach, and, lastly, also in the examination of plants and animals, or parts of them, for their inorganic constituents, I will here point out the processes best adapted to lead to the attainment of the object in view, both in the general way and in special cases.

1. *General Rules for the Detection of Inorganic Substances in Presence of Organic Matters, which by their Color, Consistence, &c., impede the Application of the Reagents, or obscure the Reactions produced.*

§ 219.

We confine ourselves here, of course, to the description of the most generally applicable methods, leaving the adaptation of the modifications which circumstances may require in special cases, to the discretion of the analyst.

1. THE SUBSTANCE UNDER EXAMINATION DISSOLVES IN WATER, BUT THE SOLUTION IS DARK COLORED OR OF SLIMY CONSISTENCE. 283

a. Boil a portion of the solution with hydrochloric acid, and gradually add chlorate of potassa, until the mixture is decolorized and perfectly fluid; heat until it no longer exhales the odor of chlorine, then dilute with water, and filter. Examine the filtrate in the usual way, commencing with § 188. Compare also § 223.

b. Boil another portion of the solution for some time with nitric acid, filter, and test the filtrate for SILVER, POTASSA, and HYDROCHLORIC ACID. If the nitric acid succeeds in effecting the ready and complete destruction of the coloring and slimy matters, &c., this method is often altogether preferable to all others.

c. ALUMINA and SESQUIOXIDE OF CHROMIUM might escape detection by this method, because ammonia and sulphide of ammonium fail to precipitate these oxides from fluids containing non-volatile organic substances. Should you have reason to suspect the presence of these oxides, deflagrate a third portion of the substance with nitrate of potassa and some carbonate of

soda, and boil the fused mass with solution of soda. The alumina is now found by acidifying with nitric acid, and then adding ammonia; the chromium—as alkaline chromate—in the filtrate, by means of acetate of lead, after addition of acetic acid.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, OR EFFECTS ONLY PARTIAL SOLUTION; THE FLUID ADMITS OF FILTRATION. 284

Filter, and treat the filtrate either as directed § 187, or, should it require decolorization, according to the directions of § 219, 1. The residue may be of various kinds.

a. IT IS FATTY. Remove the fatty matters by means of ether, and should a residue be left, treat this as directed § 173.

b. IT IS RESINOUS. Use alcohol instead of ether, or apply both liquids successively.

c. IT IS OF A DIFFERENT NATURE, *e.g.*, woody fibre, &c.

α. Dry, and ignite a portion of the dried residue in a porcelain or platinum vessel, until total or partial incineration is effected; boil the residue with nitric acid and water, and examine the solution as directed § 187, III. (109); if a residue has been left, treat this according to the directions of § 201.

β. Examine another portion for the heavy metals, in the manner directed § 219, 1, *a*; since in *a*, besides the compounds of mercury which may be present, arsenic, cadmium, zinc, &c., may volatilize.

γ. Test the remainder for ammonia, by triturating it together with hydrate of lime.

3. THE SUBSTANCE DOES NOT ADMIT OF FILTRATION OR ANY OTHER MEANS OF SEPARATING THE DISSOLVED FROM THE UNDISSOLVED PART. 285

Treat the substance in the same manner as the residue in 2. As regards the charred mass (2 *a*), it is often desirable to boil the mass, carbonized at a gentle heat, with water, filter, examine the filtrate, wash the residue, incinerate it, and examine the ash.

2. *Detection of Inorganic Poisons in Articles of Food, in Dead Bodies, &c., in Chemico-legal Cases.**

§ 220.

The chemist is sometimes called upon to examine an article of food, the contents of the stomach of an individual, a dead body, &c., with a view to detect the presence of some poison, and thus to establish the fact of a wilful or accidental poisoning; but it is more frequently the case that the question put to him is of a less general nature, and that he is called upon to determine whether a certain substance placed before him contains a *metallic* poison; or, more pointedly still, whether it contains arsenic, or hydrocyanic acid, or some other particular poison—as it may be that the symptoms 286

* Compare: *a. Fresenius,* "die Stellung des Chemikers bei gerichtlich chemischen Untersuchungen," &c. (Annal. der Chemie und Pharm. 49, 275); and *b. Fresenius* and *v. Babo's* "Abhandlung über ein neues, unter allen Umständen sicheres Verfahren zur Ausmittelung und quantitativen Bestimmung des Arsens bei Vergiftungsfällen."—Annal. der Chemie und Pharmacie, 49, 287.

point clearly in the direction of that poison, or that the examining magistrate has, or believes he has, some other reason to put this question.

It is obvious that the task of the chemist will be the easier, the more special and pointed the question which is put to him. However, the analyst will always act most wisely, even in cases where he is simply requested to state whether *a certain poison, e. g.* arsenic, is present or not, if he adopts a course of proceeding which will not only permit the detection of the *one* poison specially named, the presence of which may perhaps be suspected on insufficient grounds, but will moreover inform him as to the presence or absence of other similar poisons.

But we must not go too far in this direction either; if we were to attempt to devise a method that should embrace *all* poisons, we might unquestionably succeed in elaborating such a method at the writing-desk; but practical experience would but too speedily convince us that the intricate complexity inseparable from such a course, must necessarily impede the easy execution of the process, and impair the certainty of the results, to such an extent indeed, that the drawbacks would be greater than the advantages derivable from it.

Moreover, the attendant circumstances permit usually at least a tolerably safe inference as to the group to which the poison belongs. Acting on these views, I give here,—

1. A method which ensures the detection of the minutest traces of arsenic, allows of its quantitative determination, and permits at the same time the detection of all other metallic poisons.

2. A method to effect the detection of hydrocyanic acid, which leaves the substance still fit to be examined both for metallic poisons and for vegeto-alkalies.

3. A method to effect the detection of phosphorus, which does not interfere with the examination for other poisons.

This Section does not, therefore, profess to supply a complete guide in every possible case or contingency of chemico-legal investigations. But the instructions given in it are the tried and proved results of my own practice and experience. Moreover, they will be found sufficient in most cases, the more so as I shall append to the Section on the vegeto-alkalies the description of a process by which the detection of these latter poisons in criminal cases may be effected.

I. Method for the Detection of Arsenic (with due Regard to the possible Presence of other Metallic Poisons.

§ 221.

Of all metallic poisons arsenic is the most dangerous, and at the same time the one most frequently used, more particularly for the wilful poisoning of others. And again, among the compounds of arsenic, arsenious acid (white arsenic) occupies the first place, because—(1) It kills even in small doses; (2) It does not betray itself, or at least very slightly, by the taste; and (3) It is but too readily procurable. 287

As arsenious acid dissolves in water only sparingly and—on account of the difficulty with which moisture adheres to it—very slowly, the greater portion of the quantity swallowed exists usually in the body still in the undissolved state; as, moreover, the smallest grains of it may be readily detected by means of an exceedingly simple experiment; and lastly, as—no matter what opinion may be entertained about the normal presence of arsenic in the bones, &c.—this much is certain, that at all events *arsenious acid in grains or powder* is never normally present in the body, the particular care and efforts of the analyst ought always to be directed to the detection of the arsenious acid in substance—and this end may indeed usually be attained.

A. Method for the Detection of undissolved Arsenious Acid.

§ 222.

1. If you have to examine some article of food, substances rejected from the stomach, or some other matter of the kind, mix the whole as uniformly as may be practicable, reserve one-third for unforeseen contingencies, and mix the other two-thirds in a porcelain dish with distilled water, with a stirring rod; let the mixture stand a little, and then pour off the fluid, together with the lighter suspended particles, into another porcelain dish. Repeat this latter operation several times, if possible, with the same fluid, pouring it from the second dish back into the first, &c. Finally, wash once more with pure water, remove the fluid, as far as practicable, and try whether you can find in the dish small, white, hard grains which feel gritty and grate under the glass rod. If not, proceed as directed § 223. But if so, put the grains, or part of them, on blotting-paper, removing them from the dish with the aid of pincers, and try the deportment of one or several grains upon heating in a glass tube, and of some other grains upon ignition with a splinter of charcoal (compare § 131, 11). If you obtain in the former experiment a white crystalline sublimate, in the latter a lustrous arsenical mirror, the fact is clearly demonstrated that the grains selected and examined consisted really of arsenious acid. If you wish to determine the quantity of the poison, unite the contents of both dishes, and proceed as directed § 223. 288

2. If a stomach is submitted to you for analysis, empty the contents into a porcelain dish, turn the stomach inside out, and (*a*), search the inside coat for small, white, hard, sandy grains. The spots occupied by such grains are often reddened; they are also frequently found firmly imbedded in the membrane. (*b*) Mix the contents in the dish uniformly, put aside one-third for unforeseen contingencies, and treat the other two-thirds as in 1. The same course is pursued also with the intestines. In other parts of the body—with the exception perhaps of the pharynx and œsophagus—arsenious acid cannot be found in grains, if the poison has been introduced through the mouth. If you have found grains of the kind described, examine them as directed in 1; if not, proceed according to the instructions of § 223.

*B. Method for the Detection of Arsenic in whatever Form of Combination it may exist, which allows also a Quantitative Determination of that Poison, and permits at the same time the Detection of other Metallic Poisons which may be present.**

§ 223.

If you have found no arsenious acid by the method described in *A*, evaporate the mass in the porcelain dish, which has been diluted by washing with water (see *A*, 1), on the water-bath, to a pasty consistence. If you have to analyze a stomach, intestinal tube, &c., cut this into pieces, and add two-thirds to the mass in the dish. 289

In examining other parts of the body (the lungs, liver, &c.), cut them also into pieces, and use two-thirds for the analysis. The process is divided into the following parts.†

1. *Decolorization and Solution.*

Add to the matters in the porcelain dish an amount of pure hydrochloric acid about equal to, or somewhat exceeding the weight of the dry substances present, and sufficient water to give to the entire mass the consistence of a thin paste. Heat the dish now on the water-bath, adding every five minutes about two grammes (half a drachm) of chlorate of potassa to the hot fluid, with stirring, and continue the same operation until the contents of the dish show a light-yellow color and a perfectly homogeneous appearance, and are quite fluid. When this point is attained, add again a portion of chlorate of potassa, and then remove the dish from the water-bath. When the contents are quite cold, transfer them cautiously to a linen strainer or to a white filter, according to the greater or less quantity of substance; allow the whole of the fluid to pass through, and put the filtrate aside. Wash the residue well with hot water, and dry it; then mark it I., and reserve for further examination, according to the instructions of § 223, 8 (303). Evaporate the washings on the water-bath to about 3 or 4 oz. (about 100 grm.), add this, together with any precipitate that may have formed therein, to the principal filtrate, and then add to the united fluid, which is still very acid, some solution of sulphite of soda, with stirring, until the odor of sulphurous acid becomes distinctly perceptible. Then heat the mixture again gently on the water-bath until the excess of the sulphurous acid is expelled, which will take about an hour. 290

2. *Treatment of the Solution with Hydrosulphuric Acid* (Separation of the Arsenic as Tersulphide, and, respectively, of all the Metals of Groups V. and VI. in form of Sulphides).

When the fluid obtained in 1, and which amounts to about twice 291

* This method is essentially the same as that which I have elaborated and published in 1844, jointly with *L. v. Babo;* compare "Annal. der Chemie und Pharmacie," Bd. 49, p. 308. I have since that time had frequent occasion to apply it; I have also had it tried by others, under my own inspection, and *I have invariably found it to answer the purpose perfectly.*

† I think I need hardly observe that in such extremely delicate experiments the vessels and reagents used in the process must be perfectly free from arsenic, from heavy metals in general, and indeed from every impurity.

or three times the quantity of hydrochloric acid used, is quite cold, pour it into a beaker, transmit through it, for about 12 hours, a slow stream of washed hydrosulphuric acid gas, rinse the delivery pipe with some ammonia, add the ammoniated solution thus obtained to the principal fluid, cover the beaker lightly with unsized paper, and put it in a moderately warm place (about 86° F.), until the odor of hydrosulphuric acid has nearly disappeared. Collect the precipitate obtained in this manner on a moderately sized filter, and wash, until the washings are quite free from chlorine. Concentrate the filtrate and washings somewhat, mix the fluid in a flask with ammonia to alkaline reaction, then with sulphide of ammonium, closely cork the flask, which must now be nearly full, and reserve for further examination according to the instructions of § 223, 9 (**307**).

3. *Purification of the Precipitate produced by Hydrosulphuric Acid.*

Thoroughly dry the precipitate obtained in 2—which, besides **292**
organic matters, must contain, in form of tersulphide, the whole of the arsenic present in the analyzed substance, as well as, in form of sulphides, all the metals of Groups V. and VI. which may happen to be present—together with the filter, in a small porcelain dish, heated on the water-bath; add pure fuming nitric acid (perfectly free from chlorine), drop by drop, until the mass is completely moistened, and then evaporate on the water-bath to dryness. Moisten the residue uniformly all over with pure hydrated sulphuric acid, previously warmed; then heat for two or three hours on the water-bath, and finally on the air- sand- or oil-bath at a somewhat higher, though still moderate temperature (338° F.), until the charred mass becomes friable, and a small sample of it—to be returned afterwards to the mass—when mixed with water and then allowed to subside, gives a colorless fluid; should the fluid standing over the sediment show a brownish tint, or the residue, instead of being friable, consist of a brown, oily liquid, add to the mass some cuttings of pure Swedish filtering paper, and continue the application of heat. By attending to these rules you will always completely attain the object in view, viz., the destruction of the organic substances, without loss of any of the metals. Warm the residue on the water-bath, with a mixture of 8 parts of water and 1 part of hydrochloric acid, filter, wash the undissolved part thoroughly with hot, distilled water, with addition of a little hydrochloric acid, and add the washings, which must be concentrated if necessary, to the filtrate.

Dry the washed carbonaceous residue, then mark it II., and reserve for further examination according to the instructions given in § 223, 8, *b* (**304**).

4. PRELIMINARY EXAMINATION FOR ARSENIC AND OTHER METALLIC POISONS OF GROUPS V. AND VI. (Second Precipitation with Hydrosulphuric Acid).

The clear fluid obtained in 3 contains all the arsenic which **293**
may have been present, in form of arsenious acid, and may con-

tain also tin, antimony, mercury, copper, bismuth, and cadmium. Supersaturate a small portion of it cautiously and gradually with a mixture of carbonate of ammonia and some ammonia, and observe whether a precipitate is thereby produced. Acidify the supersaturated sample of the fluid with hydrochloric acid, which will redissolve the precipitate that may have been produced by ammonia; then return the sample to the fluid, and treat the latter with hydrosulphuric acid in strict accordance with the directions of 2 (**291**).

This process may lead to three different results, which are to be carefully distinguished.

a. The hydrosulphuric acid fails to produce a precipitate; **294** but subsequently, after the fluid treated as directed in 2 (**291**) has stood for some time, a trifling white or yellowish-white precipitate separates. In this case probably no metals of Groups V. and VI. are present. Nevertheless, treat the filtered and washed precipitate as directed in 5 (**297**), to guard even against overlooking the minutest traces of arsenic, &c.

b. A precipitate is formed, of a pure yellow color like that **295** of tersulphide of arsenic. Take a small portion of the fluid, together with the precipitate suspended therein, add some ammonia, and shake the mixture for some time, without application of heat. If the precipitate dissolves readily and, with the exception of a trace of sulphur, completely, and if, in the preliminary examination (**293**), carbonate of ammonia has failed to produce a precipitate, arsenic alone is present, and no other metal (tin or antimony), at all events, no quantity worth mentioning. Mix the solution of the small sample in ammonia with hydrochloric acid to acid reaction, return the acidulated sample to the fluid from which it was taken, and which contains the yellow precipitate produced by the hydrosulphuric acid, and proceed as directed in 5 (**297**). If, on the other hand, the addition of ammonia to the sample completely or partially fails to redissolve the precipitate, or if, in the preliminary examination (**293**), carbonate of ammonia has produced a precipitate, there is reason to suppose that another metal is present, perhaps with arsenic. In this latter case also, add to the sample in the test-tube hydrochloric acid to acid reaction, return the acidulated sample to the fluid from which it was taken, which contains the yellow precipitate produced by the hydrosulphuric acid, and proceed as directed in 6 (**298**).

c. A precipitate is formed, which is not yellow. In that **296** case you have to assume that other metals are present, perhaps with arsenic. Proceed as directed in 6 (**298**).

5. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid, in Cases where the Results of the Examination in* 4 *b* (**295**) *lead to the Assumption that Arsenic alone is present.* Determination of the Weight of the Arsenic.

As soon as the fluid precipitated according to the directions of **297** 4 (**293**) has nearly lost the smell of sulphuretted hydrogen transfer

the yellow precipitate to a small filter, wash thoroughly, pour upon the still moist precipitate solution of ammonia, and wash the filter—on which, in this case, nothing must remain undissolved, except sulphur—thoroughly with dilute ammonia; evaporate the ammoniacal fluid in a small, accurately tared porcelain dish, on the water-bath, dry the residue at 212° F. until its weight suffers no further diminution, and weigh. If it is found, upon reduction, that the residue consisted of perfectly pure tersulphide of arsenic, calculate for every part of it 0·8049 of arsenious acid, or 0·6098 of arsenic. Treat the residue in the dish according to the instructions given in 7 (**300**).

6. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid, in Cases where the Results of the Examination in 4, b* (**295**), *or in 4, c* (**296**), *lead to the Assumption that another Metal is present—perhaps with Arsenic.* Separation of the Metals from each other. Determination of the Weight of the Arsenic.

If you have reason to suppose that the precipitate produced by **298**
hydrosulphuric acid (**293**) contains other metals, perhaps with arsenic, proceed as follows:—As soon as the precipitation is thoroughly accomplished, and the smell of sulphuretted hydrogen nearly disappeared, pour the precipitate on a small filter, wash thoroughly, perforate the point of the filter, and rinse the contents with the washing-bottle into a little flask, using the least possible quantity of water for the purpose; add to the fluid in which the precipitate is now suspended, first ammonia, then some yellowish sulphide of ammonium, and let the mixture digest for some time at a gentle heat. Should part of the precipitate remain undissolved, filter this off, wash, perforate the filter, rinse off the residuary precipitate, mark it III., and reserve for further examination according to the instructions given in § 223, 8, *c* (**305**). Evaporate the filtrate, together with the washings, in a small porcelain dish, to dryness. Treat the residue with some pure fuming nitric acid (free from chlorine), nearly expel the acid by evaporation, and then add, as *C. Meyer* was the first to recommend, gradually, and in small portions at a time, a solution of pure carbonate of soda until it predominates. Add now a mixture of 1 part of carbonate and 2 parts of nitrate of soda, in sufficient, yet not excessive quantity, evaporate to dryness, and heat the residue very gradually to fusion. Let the fused mass cool, and, when cold, extract it with cold water. If a residue remains undissolved, filter, wash with a mixture of equal parts of spirit **299**
of wine and water, mark it IV., and reserve for further examination, according to the directions of § 223, 8, *d* (**306**). Mix the solution, which must contain all the arsenic as arsenate of soda, with the washings, previously freed from alcohol by evaporation, add gradually and cautiously pure dilute sulphuric acid to strongly acid reaction, evaporate in a small porcelain dish, and, when the fluid is tolerably concentrated, add again sulphuric acid, to see whether the quantity first added has been sufficient to expel all nitric and nitrous acids; heat now very cautiously until heavy fumes of hydrated sulphuric acid begin to escape; then let the liquid cool,

and, when cold, add a little of a concentrated solution of sulphurous acid in water; warm until the excess of the sulphurous acid is driven off, and then conduct hydrosulphuric acid into the fluid. If arsenic is present, a yellow precipitate will form. When the precipitate has completely subsided, and the fluid has nearly lost the smell of sulphuretted hydrogen, filter, wash the precipitate, dissolve it in ammonia, and proceed with the solution as directed in 5, (**297**), to determine the weight of the arsenic.

7. *Reduction of the Sulphide of Arsenic.*

The production of metallic arsenic from the sulphide, which may **300**
be regarded as the keystone of the whole process, demands the greatest care and attention. The method recommended in § 131, 12, viz., to fuse the arsenical compound, mixed with cyanide of potassium and carbonate of soda, in a slow stream of carbonic acid gas, is the best and safest, affording, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with some other body, more particularly antimony; on which account it is more especially adapted for medico-legal investigations.

As regards the process of reduction, either proceed at once with the sulphide of arsenic, or previously convert the latter into arsenic acid (see 301). In the former case take care, if possible, not to use the whole of the residue in the dish, obtained by the evaporation of the ammoniacal solution, but only a portion of it, so that the process may be repeated several times, if necessary. Should the residue be too trifling to admit of being divided into several portions, dissolve it in a few drops of ammonia, add a little carbonate of soda, and evaporate on the water-bath to dryness, taking care to stir the mixture during the process; divide the dry mass into several portions, and proceed to reduction.

*Otto** recommends to convert the sulphide first into arsenic acid, **301**
and then to reduce the latter with cyanide of potassium. The following is the process given by him to effect the conversion of the sulphide into the acid; pour concentrated nitric acid over the sulphide of arsenic in the dish, evaporate, and repeat the same operation several times, if necessary, and then remove every trace of nitric acid by repeatedly moistening the residue with water, and drying again; when the nitric acid is *completely* expelled, treat the residue with a few drops of water, add carbonate of soda in powder, to form an alkaline mass, and thoroughly dry this in the dish, with frequent stirring, taking care to collect the mass within the least possible space in the middle of the dish. The dry mass thus obtained is admirably adapted for reduction. I can, from the results of my own experience, fully confirm this statement of *Otto;* but I must once more repeat, that it is indispensable for the success of the operation that the residue should be perfectly free from *every trace* of nitric acid or nitrate; otherwise deflagration is sure to take place during the process of fusion with cyanide of potassium, and, of course, the experiment will fail.

* "Anleitung zur Ausmittelung der Gifte," *von Dr. Fr. Jul. Otto*, p. 36.

When the operation is finished, cut off the reduction tube at *c* (see 302
Fig. 30), set aside the fore part, which contains the arsenical mirror, put the other part of the tube into a cylinder, pour water over it, and let it stand some time; then filter the solution obtained, add to the

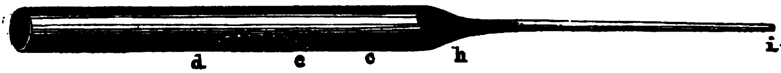

Fig. 30.

filtrate hydrochloric acid to acid reaction; then again some hydrosulphuric acid, and observe whether this produces a precipitate. In cases where the reduction of the sulphide of arsenic has been effected in the direct way, without previous conversion to arsenic acid, a trifling yellow precipitate will usually form; had traces of antimony been present, the precipitate would be orange-colored and insoluble in carbonate of ammonia. When all the soluble salts of the fused mass have been dissolved out, examine the metallic residue, which may be left behind, according to the directions of § 133, 1, for traces of tin and antimony; these being the only metals that can possibly be present if the instructions here given have been strictly followed. Should *appreciable* traces of these metals, or of either of them, be found, proper deduction and correction must be made in calculating the weight of the arsenic.

8. *Examination of the reserved Residues, marked severally* I., II., III., *and* IV., *for other Metals of the Fifth and Sixth Groups.*

a. Residue I. Compare § 223, 1 (290).

This may contain chloride of silver and sulphate of lead, 303
possibly also binoxide of tin. Incinerate the residue (I.) in a porcelain dish, burn the carbon with the aid of some nitrate of ammonia, extract the residue with water, dry the part left undissolved, and then fuse it with cyanide of potassium in a porcelain crucible. When the fused mass is cold, treat it with water until all that is soluble in it is completely removed; warm the residue with nitric acid, and proceed as directed in § 179.

b. Residue II. Compare § 223, 3 (292).

The carbonaceous residue which is obtained by the purifica- 304
tion of the crude sulphide by means of nitric acid and sulphuric acid, may more particularly contain lead, mercury, and tin; antimony and bismuth may also be present.

Heat the residue for some time with nitrohydrochloric acid, and filter the solution; wash the undissolved residue with water mixed with some hydrochloric acid, add the washings to the filtrate, and treat the dilute fluid thus obtained with hydrochloric acid; should a precipitate form, examine this according to the instructions given in § 189. Incinerate the residue insoluble in nitrohydrochloric acid, fuse the ash in conjunction with cyanide of potassium, and proceed with the fused mass as directed in 8, *a* (303).

c. Residue III. Compare § 223, 6 (**298**).

Examine the precipitate insoluble in sulphide of ammonium for the metals of the fifth group according to the instructions given in § 191. **305**

d. Residue IV. Compare § 223, 6 (**299**). **306**

This may contain tin and antimony, perhaps also copper. Proceed as directed § 190, 2, *b* (**123**). If the color of the residue was black (oxide of copper), treat the reduced metals according to the instructions given in § 179.

9. *Examination of the Filtrate reserved in* § 233, 2 (**291**), *for Metals of the Fourth and Third Groups, especially for Zinc and Chromium.*

a. As we have seen in § 223, 2 (**291**), the fluid filtered from the precipitate produced by hydrosulphuric acid, and temporarily reserved for further examination, has already been mixed with sulphide of ammonium. The addition of this reagent to the filtrate is usually attended with the formation of a precipitate, consisting of sulphide of iron and phosphate of lime, but which may possibly also contain sulphide of zinc. Filter the fluid from this precipitate, and treat the filtrate as directed in *b* (**308**); wash the precipitate with water mixed with some sulphide of ammonium, dissolve by warming with hydrochloric acid, and boil the solution with nitric acid, to convert the protoxide of iron into sesquioxide; add, if necessary, sufficient sesquichloride of iron for carbonate of soda to produce a brownish-yellow precipitate in a sample of the fluid; neutralize almost completely with carbonate of soda, precipitate with carbonate of baryta, and filter; the precipitate contains all the sesquioxide of iron and all the phosphoric acid. Concentrate the filtrate, precipitate the baryta with dilute sulphuric acid, filter, add to the filtrate ammonia to alkaline reaction, and precipitate with sulphide of ammonium the zinc which may be present. For the further examination of the precipitate, see § 105. **307**

b. If the analyzed substance contained chromium, this will be found in the fluid filtered from the precipitate produced by sulphide of ammonium, § 223, 2 (**291**). Compare § 223, 9, *a* (**307**). If you wish to ascertain whether chromium is really present, evaporate the filtrate to dryness, mix the residue with 3 parts of nitrate of potassa and 1 part of carbonate of soda, put the mixture into a Hessian crucible and heat to moderate redness. Allow the fused mass to cool, and, when cold, boil with water: yellow coloration of the fluid shows the presence of alkaline chromate, and accordingly of chromium. For confirmatory tests, see § 138. **308**

II. Method for the Detection of Hydrocyanic Acid.

§ 224.

In cases of actual or suspected poisoning with hydrocyanic acid, **309**

where it is required to separate that acid from articles of food or from the contents of the stomach, and thus to prove its presence, it is highly necessary to act with the greatest expedition, as the hydrocyanic acid speedily undergoes decomposition. Still this decomposition is not quite so rapid as is generally supposed, and indeed it requires some time before the *complete* decomposition of the *whole* of the acid present is effected.*

Although hydrocyanic acid betrays its presence, even in minute quantities, by its peculiar odor, still this sign must never be looked upon as conclusive. On the contrary, to adduce positive proof of the presence of the acid, it is always indispensable to separate it, and to convert it into certain known compounds.

The method of accomplishing this is based upon distillation of the acidified mass, and examination of the distillate for hydrocyanic acid. Now, as the non-poisonous salts, ferro- and ferricyanide of potassium, on distillation, likewise yield a distillate containing hydrocyanic acid, it is, of course, indispensable—as *Otto* very properly observes—first to ascertain whether one of these salts may not be present. For this purpose, stir a small portion of the mass to be examined with water, filter, acidify the filtrate with hydrochloric acid, and test a sample of it with sesquichloride of iron, another with sulphate of protoxide of iron. If no blue precipitate forms in either, soluble ferro- and ferricyanides are not present, and you may safely proceed as follows:

Test, in the first place, the reaction of the mass under examina- 310
tion; if necessary, after mixing and stirring it with water. If it is not already strongly acid, add solution of tartaric acid until the fluid strongly reddens litmus paper; introduce the mixture into a retort, and place the body of the retort, with the neck pointing upwards, in an iron or copper vessel, but so that it does not touch the bottom, which should, moreover, by way of precaution, be covered with a cloth; fill the vessel with a solution of chloride of calcium, and apply heat, so as to cause gentle ebullition of the contents of the retort. Conduct the vapors passing over, with the aid of a tight-fitting tube, bent at a very obtuse angle, through a *Liebig's* condensing apparatus, and receive the distillate in a small, weighed flask. When about half-an-ounce of distillate has passed over, remove the receiver, and replace it by a somewhat larger flask, also previously tared. Weigh the contents of the first receiver, and proceed as follows:

a. Mix one-fourth of the distillate with solution of potassa 311
or soda to strongly alkaline reaction, and then add a small quantity of solution of sulphate of protoxide of iron, mixed with a little sesquichloride of iron.

b. Treat another fourth as directed § 155, 7, to convert the 312
hydrocyanic acid into sulphocyanide of iron. As the distillate might, however, contain acetic acid, do not neglect to add some

* Thus I succeeded in separating a notable quantity of hydrocyanic acid from the stomach of a man who had poisoned himself with that acid in very hot weather, and whose intestines were handed to me full 36 hours after death.—A dog was poisoned with hydrocyanic acid, and the contents of the stomach, mixed with the blood, were left for 24 hours exposed to an intense summer-heat, and then examined: the acid was still detected.

hydrochloric acid after the sesquichloride of iron, in order to neutralize the adverse influence of the acetate of ammonia. Compare § 155, 7.

c. If the experiments *a* and *b* have demonstrated the pre- 313
sence of hydrocyanic acid, and you wish now also to approximately determine its quantity, continue the distillation, until the fluid passing over contains no longer the least trace of hydrocyanic acid; add one-half of the contents of the second receiver to the remaining half of the contents of the first, mix the fluid with nitrate of silver, then with ammonia until it predominates, and finally with nitric acid to strongly acid reaction. Allow the precipitate which forms to subside, filter on a tared filter, dried at 212° F., wash the precipitate, dry it thoroughly at 212° F., and weigh. Ignite the weighed precipitate in a small porcelain crucible, to destroy the cyanide of silver, fuse the residue with carbonate of soda and potassa—to effect the decomposition of the chloride of silver which it may contain—boil the mass with water, filter, acidify the filtrate with nitric acid, and precipitate with nitrate of silver; determine the weight of the chloride of silver which may precipitate, and deduct the amount found from the total weight of the chloride and cyanide of silver: the difference gives the quantity of the latter; by multiplying the quantity found of the cyanide of silver by 0·2017, you find the corresponding amount of anhydrous hydrocyanic acid; and by multiplying this again by 2—as only one-half of the distillate has been used—you find the total quantity of hydrocyanic acid which was present in the examined mass.

Instead of pursuing this indirect method, you may also deter- 314
mine the quantity of the hydrocyanic acid by the following direct method: Introduce half of the distillate into a retort, together with powdered borax; distil to a small residue, and determine the hydrocyanic acid in the distillate as cyanide of silver. Hydrochloric acid can no longer be present in this distillate, as the soda of the borax retains it in the retort (*Wackenroder*).

III. Method for the Detection of Phosphorus.

§ 225.

Since phosphorus paste has been employed to poison mice, &c., 315
and the poisonous action of lucifer matches has become more extensively known, phosphorus has not unfrequently been resorted to as an agent for committing murder. The chemist is therefore occasionally called upon to examine some article of food, or the contents of a stomach, for this substance. It is obvious that, in cases of the kind, his whole attention must be directed to the separation of the phosphorus in the *free state*, or to producing such reactions as will enable him to infer the presence of *free phosphorus;* since the mere finding of phosphorus in form of phosphates would prove nothing, as phosphates invariably form constituents of animal and vegetable bodies.

E. Mitscherlich, who has published the latest treatise on the subject,* recommends the following method as the simplest and best:† 316

Mix the substance under examination with water and some sulphuric acid, and subject the mixture to distillation in a flask, A (see Fig. 31). This flask is connected with an evolution tube, *b*, and

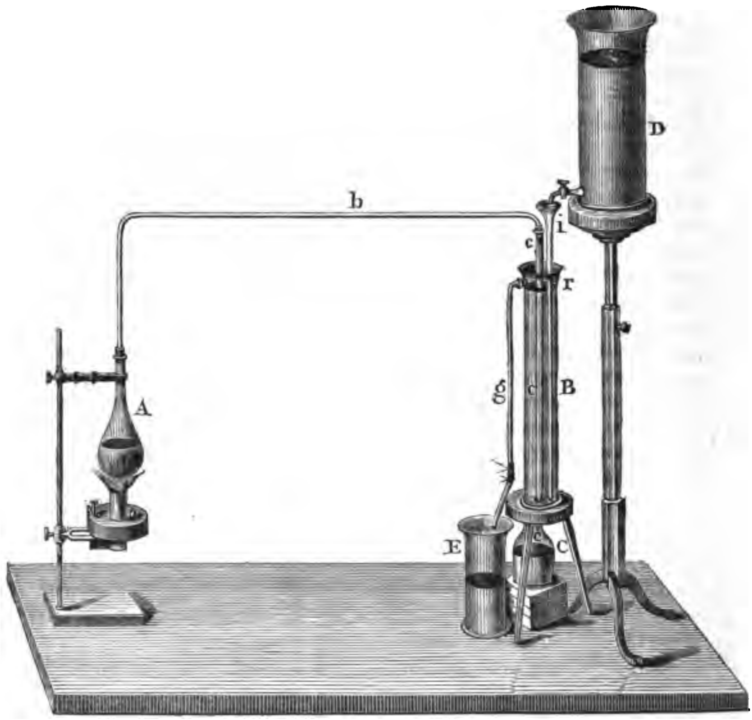

Fig. 31.

the latter again with a glass cooling or condensing tube, *c c c*, which passes through a perforated cork *a*, in the bottom of a cylinder, B, into a glass vessel, C. Cold water runs from D, through a stopcock, into a funnel, *i*, which extends to the bottom of B; the warmed water flows off through *g*.

Now, if the substance in A contains phosphorus, there will appear, in the dark, in the upper part of the condensing tube at the point *r*, where the aqueous vapors distilling over enter that part of the tube, a strong luminosity, usually a luminous ring. If you take for distillation 5 oz. of a mixture containing only $\frac{1}{40}$th of a grain of phosphorus, and accordingly only 1 part of

* "Journal für prakt. Chemie," vol. 66, p. 238.
† I have tried this method, and found it to answer perfectly.

phosphorus in 100,000 parts of mixture, you may distil over 3 oz. of it—which will take at least half-an-hour—without the luminosity ceasing; *Mitscherlich*, in one of his experiments, stopped the distillation after half-an-hour, allowed the flask to stand uncorked a fortnight, and then recommenced the distillation: the luminosity was as strong as at first. If the fluid contains substances which prevent the luminosity of phosphorus in general, such as ether, alcohol, or oil of turpentine, no luminosity is observed so long as these substances continue to distil over. In the case of ether and alcohol, however, this is soon effected, and the luminosity accordingly very speedily makes its appearance; but it is different with oil of turpentine, which exercises a lasting preventive influence upon the manifestation of this reaction.

After the termination of the process, globules of phosphorus 317
are found at the bottom of the receiver, C. *Mitscherlich* obtained from 5 oz. of a mixture containing $\frac{1}{3}$ grain of phosphorus, so many globules of that body that the one-tenth part of them would have been amply sufficient to demonstrate its presence. In medico-legal investigations these globules should first be washed with alcohol, and then weighed. A portion may afterwards be subjected to a confirmatory examination, to make quite sure that they really consist of phosphorus: the remainder, together with a portion of the fluid which shows the luminosity upon distillation, should be sent in with the report.

3. *Examination of the Inorganic Constituents of Plants, Animals, or Parts of the same, of Manures, &c. (Analysis of Ashes.)*

§ 226.

A. Preparation of the Ash.

It is sufficient for the purposes of a qualitative analysis to in- 318
cinerate a comparatively small quantity of the substance which it is intended to examine for its inorganic constituents; the substance must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but it may be conducted also in a Hessian crucible placed in a slanting position, or, under certain circumstances, even in a small porcelain or platinum dish. The heat must always be moderate, to guard against the volatilization of certain constituents, more especially of metallic chlorides. It is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as, *e. g.* the ash of beetroot molasses, it is even advisable to effect, in the first place, complete carbonization, then to boil the charred mass with water, and finally to incinerate the washed and dried residue. For further particulars see *Quantitative Analysis*, 3rd Edition, § 250.

B. Examination of the Ash.

As the qualitative analysis of the ash of a vegetable substance 319
is usually undertaken, either as a practical exercise, or for the purpose of determining its general character, and the state or condition in which any given constituent may happen to be pre-

sent, or also with a view to make, as far as practicable, an approximate estimation of the respective quantities of the several constituents, it is usually the best way to examine separately; (1) the part soluble in water; (2) the part soluble in hydrochloric acid; and (3) the residue which is insoluble in either menstruum. This can be done the more readily, as the number of bodies to which regard must be had in the analysis is only small, and the several processes may accordingly be expeditiously performed.

a. Examination of the Part soluble in Water.

Boil the ash with water, filter, and whilst the residue is being washed, examine the solution as follows:—

1. Add to a portion, after heating it, hydrochloric acid in excess, **320** warm, and let the fluid stand at rest. Effervescence indicates CARBONIC ACID, combined with alkalies; odor of hydrosulphuric acid indicates the SULPHIDE of an ALKALI METAL, formed from an alkaline sulphate by the reducing action of the carbon. Turbidity from separation of sulphur, with odor of sulphurous acid, denotes a HYPOSULPHITE (which occurs occasionally in the ash of coal). Filter, if necessary, and add to the filtrate—or to the fluid if no filtration is required—some chloride of barium; the formation of a white precipitate indicates the presence of SULPHURIC ACID.

2. Evaporate another portion of the solution until it is reduced **321** to a small volume, add hydrochloric acid to acid reaction—effervescence indicates the presence of CARBONIC ACID—evaporate now to dryness, and treat the residue with hydrochloric acid and water. The portion left undissolved consists of SILICIC ACID. Filter, add ammonia, chloride of ammonium, and sulphate of magnesia; the formation of a white precipitate indicates the presence of PHOSPHORIC ACID. Instead of this reaction, you may also mix the fluid filtered from the silicic acid with acetate of soda, and then cautiously add, drop by drop, sesquichloride of iron, or you may test with molybdate of ammonia (§ 143).

3. Add to another portion of the solution nitrate of silver as **322** long as a precipitate continues to form; warm gently, and then cautiously add ammonia: if a black residue is left, this consists of sulphide of silver, proceeding from the sulphide of an alkali metal, or from a hyposulphite. Mix the ammoniacal solution now—after previous filtration if necessary—cautiously with nitric acid until it is exactly neutralized. If this produces a *bright yellow* precipitate, the phosphoric acid found in 2 was present in the tribasic, if a *white* precipitate, it was present in the bibasic form. Add more nitric acid. This effects the solution of the phosphate of silver precipitate. But if CHLORINE (iodine,* bromine) is present, a portion of the precipitate remains undissolved, or the fluid appears turbid.

4. Acidify a portion of the solution with hydrochloric acid, and **323** then make it alkaline with ammonia; mix the alkaline fluid with oxalate of ammonia, and let it stand at rest. The formation of a

* To detect the iodine in aquatic plants, dip the plant in a weak solution of potassa (*Chatin*), dry, incinerate, treat with water, and examine the aqueous solution as directed § 211, 2, *c*, *β*, *aa* (**258**).

white precipitate indicates LIME. Filter, and mix the filtrate with ammonia and phosphate of soda; the formation of a crystalline precipitate, which often becomes visible only after long standing, indicates MAGNESIA. Magnesia is often found in distinctly appreciable, lime only in exceedingly minute, quantity, even when alkaline carbonates and phosphates are present.

5. For POTASSA and SODA examine as directed § 195.

b. Examination of the Part soluble in Hydrochloric Acid.

Warm the residue left undissolved by water with hydrochloric 324 acid*—effervescence indicates CARBONIC ACID, combined with alkaline earths; evolution of chlorine denotes OXIDES OF MANGANESE—evaporate to dryness, and heat a little more strongly, to effect the separation of the silicic acid; moisten the residue with hydrochloric acid and some nitric acid, add water, warm, and filter.

1. Test with hydrosulphuric acid. If this produces any other than a perfectly white precipitate, you must examine it in the usual way. The ashes of plants occasionally contain COPPER; if the plant has been manured with excrements deodorized by nitrate of lead, they may contain LEAD; other metals are also occasionally found.

2. Mix a portion of the original solution with carbonate of soda, 325 as long as the precipitate formed redissolves upon stirring; then add acetate of soda, and some acetic acid. This produces, in most cases, a white precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON. If the fluid in which this precipitate is suspended is reddish, there is more sesquioxide of iron present than corresponds to the phosphoric acid; if it is colorless, add sesquichloride of iron, drop by drop, until the fluid looks reddish. (From the quantity of the precipitate of phosphate of sesquioxide of iron formed you may estimate the PHOSPHORIC ACID present.) Heat to boiling,† filter hot, and mix the filtrate, after addition of ammonia, with yellowish sulphide of ammonium, in a stoppered flask; should a precipitate form, after long standing, examine this before the blowpipe for MANGANESE, and the fluid filtered from it for LIME and MAGNESIA, in the usual way (§ 226, B, *a*, 4 [323]).

c. Examination of the Residue insoluble in Hydrochloric Acid.

The residue insoluble in hydrochloric acid contains,

1. The silicic acid, which has separated on treating with hydro- 326 chloric acid.

2. Those ingredients of the ash which are insoluble in hydrochloric acid. These are, in most ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stems of cereals and others abounding in silicic acid, that are not completely decomposed by hydrochloric acid.

* If the residue still contains much carbon, after further incineration.

† If this should fail to decolorize the fluid, add some more acetate of soda.

Boil the washed residue with solution of carbonate of soda in excess, filter hot, wash with boiling water, and test for silicic acid in the filtrate by evaporation with hydrochloric acid. If the ash was of a kind to be completely decomposed by hydrochloric acid, the analysis may be considered as finished—for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant a more minute examination by fluxing. But, if the ash abounded in silicic acid, and it may therefore be supposed that the hydrochloric acid has failed to effect complete decomposition, evaporate half of the residue insoluble in solution of carbonate of soda, with pure solution of soda in excess, in a silver or platinum dish, to dryness. This decomposes the silicates of the ash, whilst but little affecting the sand. Acidify now with hydrochloric acid, evaporate to dryness, &c., and proceed as in *b* (**324**). For the detection of the alkalies use the other half of the residue. Compare § 205, 2 (**228**). **327**

SECTION III.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. Additional Remarks to the Preliminary Examination.

To §§ 173—176.

THE inspection of the physical properties of a body may, as already stated § 173, in many cases enable the analyst to draw certain general inferences as to its nature. Thus, for instance, if the analyst has a white substance before him, he may at once conclude that it is not cinnabar, or if a light substance, that it is not a compound of lead, &c.

Inferences of this kind are quite admissible to a certain extent; but if carried too far, they are apt to mislead the operator, by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, platinum foil or small iron spoons may also be used in the process; however, the experiment in the glass tube gives, in most cases, results more clearly evident, and affords, moreover, the advantage that volatile bodies are less likely to escape detection, and that a more correct and precise notion can be formed of the nature of the heated substance, than exposure on platinum foil or in an iron spoon will permit. In the case of minerals it is always advisable to extend the examination in the dry way, also to fluorine (§ 147, 8). To ascertain the products of oxidation of a body, it is sometimes advisable also to heat it in a short glass-tube, open at both ends, and held in a slanting position; small quantities of a metallic sulphide, for instance, may be readily detected by this means. (Compare § 156, 6.)

With respect to the preliminary examination by means of the blow-

pipe, I have to remark that the student must avoid drawing positive conclusions from pyrochemical experiments, until he has acquired some practice in this branch of analytical chemistry. A slight incrustation of the charcoal support, which may *seem* to denote the presence of a certain metal, is not always a *conclusive* proof of the presence of that metal; nor would it be safe to assume the absence of a substance simply because the blowpipe flame fails to effect reduction, or solution of nitrate of protoxide of cobalt fails to impart a color to the ignited mass, &c. The blowpipe reactions are, indeed, in most cases, unerring, but it is not always easy to produce them, and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination; the notion that this omission will save time and trouble, is very erroneous.

II. Additional Remarks to the Solution of Substances, etc.

To §§ 177—179.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from *sparingly* soluble to *insoluble* is very gradual. Sulphate of lime, which is soluble in 430 parts of water, might perhaps serve as a limit between the two classes, since this salt may still be positively detected in aqueous solution, by the delicate reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon platinum foil, to see whether it holds a solid body in solution, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance; in cases of the kind test, in the first place, the reaction of the fluid with litmus papers; in the second place, add to a portion of it a drop of solution of chloride of barium; and lastly, to another portion some carbonate of soda. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not examine it any further for bases or acids; since if the fluid contained any of those bases or acids which principally form sparingly soluble compounds, the chloride of barium and the carbonate of soda would have revealed their presence. The analyst may therefore feel assured that the detection of the substance of which the residue left upon evaporation consists, will be more readily effected in the class of bodies insoluble in water.

If water has dissolved any part of the substance under examination, the student will always do well to examine the solution both for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound—an advantage which will amply counterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances (with few exceptions) are insoluble in water, but soluble in hydrochloric acid or in nitric acid: the phosphates, arsenates, arsenites, borates, carbonates, and oxalates of the earths and metals; and also several tartrates, citrates, malates, benzoates, and succinates; the oxides and sulphides of the heavy metals; alumina, magnesia; many of the metallic iodides and cyanides, &c. Nearly the whole of these

compounds are, indeed, decomposed, if not by dilute, by boiling concentrated hydrochloric acid;* but this decomposition gives rise to the formation of insoluble compounds when oxide of silver is present, and of sparingly soluble compounds in the presence of suboxide of mercury and lead. This is not the case with nitric acid, and accordingly the latter effects complete solution in many cases where hydrochloric acid has left a residue. But, on the other hand, nitric acid leaves, besides the bodies insoluble in any simple acid, teroxide of antimony, binoxide of tin, binoxide of lead, &c., undissolved, and fails also to effect the complete solution of many other substances.

Substances not soluble in water are, therefore, treated as follows: try to dissolve them in dilute or concentrated hydrochloric acid, cold or boiling; if this fails to effect complete solution, try to dissolve a fresh portion in nitric acid; if this also fails, treat the body with aqua regia, which is an excellent solvent, more particularly for metallic sulphides. To examine separately the solution in hydrochloric acid or in nitric acid, on the one hand, and that in nitrohydrochloric acid on the other, is, in most cases, unnecessary.

With regard to the solution of metals and alloys, I have to remark that, upon boiling them with nitric acid, white precipitates will frequently form, although neither tin nor antimony be present. Inexperienced students often confound such precipitates with the oxides of these two metals, although their appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water. Consequently the analyst should ascertain whether these white precipitates will dissolve in water or not, before he concludes them to consist of tin or antimony.

III. Additional Remarks to the Actual Examination.

To §§ 180—201.

A. General Review and Explanation of the Analytical Course.

a. DETECTION OF THE BASES.

The classification of the bases into groups, and the methods which serve to detect and isolate them individually, have been fully explained in Part I., Section III. The systematic course of analysis, from § 180 to § 196, is founded upon this classification of the bases; and as a correct apprehension of it is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests. Respecting the detection of the several bases individually, I refer the student to the recapitulations and remarks in §§ 91, 98, 102, 111, 117, 122, 127, and 133.

The general reagents which serve to divide the bases into principal groups are—HYDROCHLORIC ACID, HYDROSULPHURIC ACID, SULPHIDE OF AMMONIUM, and CARBONATE OF AMMONIA; this is likewise the order of succession in which they are applied. Sulphide of ammonium performs a *double* part.

Let us suppose we have in solution the whole of the bases, together

* For the exceptions, see § 201.

with arsenious and arsenic acids, and also phosphate of lime—which latter may serve as a type for the salts of the alkaline earths, soluble in acids, and reprecipitated unaltered by ammonia.

Chlorine forms insoluble compounds only with silver and mercury; chloride of lead is sparingly soluble in water. The insoluble subchloride of mercury corresponds to the suboxide of that metal. If, therefore, we add to our solution:

1. *Hydrochloric Acid,*

we remove from it the metallic oxides of the first division of the fifth group, viz., the whole of the OXIDE OF SILVER and the whole of the SUBOXIDE OF MERCURY. From concentrated solutions, a portion of the LEAD may likewise precipitate as chloride; this is, however, immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Hydrosulphuric acid completely precipitates the oxides of the fifth and sixth group from solutions containing a free mineral acid, since the affinity of the metallic radicals of these oxides for sulphur, and that of the hydrogen for oxygen, are sufficiently powerful to overcome the affinity between the metal and the oxygen, and that between the oxide and a strong acid, EVEN THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other bases are precipitated under these circumstances, since those of the first, second, and third group form no sulphur compounds insoluble in water; and the affinity which the metallic radicals of the oxides of the fourth group possess for sulphur, combined with that manifested by hydrogen for oxygen, is not sufficiently powerful to overcome the affinity of the metal for oxygen and of the oxide for a strong acid, IF THE LATTER IS PRESENT IN EXCESS.

If, therefore, after the removal of the oxide of silver and suboxide of mercury, by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. *Hydrosulphuric Acid,*

we remove from it the remainder of the oxides of the fifth, together with those of the sixth group, viz., OXIDE OF LEAD, OXIDE OF MERCURY, OXIDE OF COPPER, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, PROTOXIDE OF TIN, BINOXIDE OF TIN, TEROXIDE OF ANTIMONY, ARSENIOUS ACID, and ARSENIC ACID. All the other oxides remain in solution, either unaltered, or reduced to a lower degree of oxidation, *e. g.*, sesquioxide of iron to protoxide; chromic acid to sesquioxide of chromium, &c.

The sulphides corresponding to the oxides of the sixth group combine with basic metallic sulphides (the sulphides of the alkali metals), and form with them sulphur salts soluble in water; while the sulphides corresponding to the oxides of the fifth group do not possess this property, or possess it only to a limited extent.* If, therefore, we treat the whole of the sulphides precipitated by hydrosulphuric acid from an acid solution, with—

* Sulphide of mercury combines with sulphide of potassium and sulphide of sodium, but not with sulphide of ammonium; sulphide of copper dissolves a little in sulphide of ammonium, but not in sulphide of potassium or sulphide of sodium.

3. *Sulphide of Ammonium* (or, in certain cases, *Sulphide of Sodium*),

the sulphides* of mercury, lead, copper, bismuth, and cadmium remain undissolved, whilst the other sulphides dissolve as double compounds of sulphide of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with SULPHIDE OF AMMONIUM (or, as the case may be, SULPHIDE OF SODIUM), and precipitate again from this solution upon the addition of an acid, either unaltered, or, as regards the protosulphide of tin, and the tersulphide of antimony, in a state of higher sulphuration—these two compounds taking up sulphur from the yellow sulphide of ammonium. The rationale of this precipitation is as follows:—The acid decomposes the sulphur salt formed. The sulphur base (sulphide of ammonium or sulphide of sodium) transposes with the constituents of the water, forming an oxygen base (oxide of ammonium or soda) and hydrosulphuric acid; the former combines with the acid added, the latter escapes, and the liberated electro-negative sulphide (sulphur acid) precipitates. If the acid is an hydracid, its radical combines with the ammonium, its hydrogen with the sulphur. Sulphur precipitates at the same time, the sulphide of ammonium containing generally an excess of that element. The analyst must bear in mind that this eliminated sulphur makes the precipitated sulphides appear of a lighter color than they are naturally.

The alkalies, the alkaline earths, alumina, and sesquioxide of chromium have remained in solution, because their sulphur compounds are soluble in water, or because their salts are not affected in the least by hydrosulphuric acid; the sulphides corresponding to the oxides of the fourth group are insoluble in water, and would have been precipitated accordingly by hydrosulphuric acid, but for the free acid present. If, therefore, this free acid is removed, *i. e.*, if the solution is made alkaline, and then treated with hydrosulphuric acid, or, what answers both purposes at once, if

4. *Sulphide of Ammonium*,

is added to the solution,* the sulphides corresponding to the oxides of the fourth group will precipitate: viz., the SULPHIDES OF IRON, MANGANESE, COBALT, NICKEL, and ZINC. But in conjunction with them, ALUMINA, SESQUIOXIDE OF CHROMIUM, and PHOSPHATE OF LIME, are thrown down, because the affinity which the oxide of ammonium possesses for the acid of the salt of alumina or of sesquioxide of chromium, or for that which keeps the phosphate of lime in solution, causes the elements of the sulphide of ammonium to transpose with those of the water, thus giving rise to the formation of oxide of ammonium and of hydrosulphuric acid. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated oxides or with the phosphate of lime,—the oxides and the lime-salt precipitate.

There remain now in solution only the alkaline earths and the alkalies. The neutral carbonates of the former are insoluble in water,

* After previous neutralization of the free acid by ammonia, to prevent unnecessary evolution of hydrosulphuric acid; and the addition also, if necessary, of chloride of ammonium, to prevent the precipitation of magnesia by ammonia.

whilst those of the latter are soluble in that menstruum. If, therefore, we now add

5. Carbonate of Ammonia,

and apply a gentle heat, in order to decompose the bicarbonates which may have formed, the whole of the alkaline earths ought to precipitate. This is, however, the case only as regards BARYTA, STRONTIA, and LIME; of magnesia we know that, owing to its disposition to form double compounds with salts of ammonia, it precipitates only in part; and that the presence of an additional salt of ammonia will altogether prevent its precipitation. To guard against any uncertainty arising from this cause, chloride of ammonium is added previously to the addition of the carbonate of ammonia, and thus the precipitation of the magnesia is altogether prevented.

We have now in solution magnesia and the alkalies. The detection of magnesia may be effected by means of phosphate of soda and ammonia; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesia is based upon the insolubility of that earth in the pure state. The substance under examination is accordingly ignited in order to expel the salt of ammonia, and the magnesia is then precipitated by means of baryta, the alkalies, together with the newly formed salt of baryta and the excess of the caustic baryta added, remaining in solution. By the addition of carbonate of ammonia, the compounds of baryta are removed from the solution, which now only contains the fixed alkalies, the salt of ammonia formed, and the excess of the salt of ammonia added. If the salts of ammonia are then removed by ignition, the residue consists of the fixed alkalies alone. This method of separating the baryta affords the advantage over that of effecting the removal of that earth by means of sulphuric acid, that the alkalies are obtained in the most convenient form for their subsequent individual detection and isolation, viz., as chlorides. But as carbonate of baryta is slightly soluble in salts of ammonia, and gives, upon evaporation with chloride of ammonium, carbonate of baryta and chloride of barium, it is usually necessary, after the expulsion of the salts of ammonia by ignition, to precipitate it once more with carbonate of ammonia, in order to obtain a solution perfectly free from baryta. Lastly, to effect the detection of the ammonia, a fresh portion of the substance must of course be taken.

b. Detection of the Acids.

Before passing on to the examination for acids and salt-radicals, the analyst should first ask himself *which* of these substances may be expected to be present, from the nature of the detected bases and the class to which the substance under examination belongs with respect to its solubility in water or acids, since this will save him the trouble of unnecessary experiments. Upon this point I refer the student to the table in Appendix IV., in which the various compounds are arranged according to their several degrees of solubility in water and acids.

The general reagents applied for the detection of the acids are, for the inorganic acids CHLORIDE OF BARIUM and NITRATE OF SILVER, for the

organic acids CHLORIDE OF CALCIUM and SESQUICHLORIDE OF IRON. It is therefore indispensable that the analyst should first assure himself whether the substance under examination contains only inorganic acids, or whether the presence of organic acids must also be looked for. The latter is invariably the case, if the body, when ignited, turns black, owing to separation of carbon.—In the examination for bases the different reagents serve to effect the actual separation of the several groups of bases from each other; but in the examination for acids they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids, in combination with soda, for instance.

Baryta forms insoluble compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boracic acid, chromic acid, oxalic acid, tartaric acid, and citric acid; fluoride of barium also is insoluble or, at least, difficultly soluble; all these compounds are soluble in hydrochloric acid, with the exception of sulphate of baryta. If, therefore, to a portion of our neutral or, if necessary, neutralized solution, we add,

1. *Chloride of Barium,*

the formation of a precipitate will denote the presence of at least one of these acids. By treating the precipitate with hydrochloric acid, we learn at once whether sulphuric acid is present or not, as all the salts of baryta being soluble in this menstruum, with the exception of the sulphate, a residue left undissolved by the hydrochloric acid can consist only of the latter salt. When sulphate of baryta is present, the reaction with chloride of barium fails to lead to the positive detection of the whole of the other acids enumerated. For upon filtering the hydrochloric solution of the precipitates and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, &c., of baryta do not always fall down again, being kept in solution by the chloride of ammonium formed. For this reason, chloride of barium cannot serve to effect the actual separation of the whole of the acids named, and except as regards sulphuric acid, we set no value upon this reagent as a means of effecting their individual detection. Still it is of great importance as a reagent, since the non-formation of a precipitate upon its application in neutral or alkaline solutions, proves at once the absence of so considerable a number of acids.

The compounds of silver with sulphur, chlorine, iodine, bromine, cyanogen, ferro- and ferricyanogen, and of the oxide of silver with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid, are insoluble in water. The whole of these compounds are soluble in dilute nitric acid, with the exception of the chloride, iodide, bromide, cyanide, ferrocyanide, ferricyanide, and sulphide of silver. If, therefore, we add to our solution, which, for the reason just now stated, must be perfectly neutral,

2. *Nitrate of Silver,*

and precipitation ensues, this shows at once the presence of one or several of the acids enumerated; chromic acid, arsenic acid, and several

others, which form colored salts with silver, may be individually recognised with tolerable certainty by the mere color of the precipitate. By treating the precipitate now with nitric acid, we see whether it contains any of the haloid compounds of silver, as these latter remain undissolved, whilst all the oxide salts dissolve.—Nitrate of silver fails to effect the complete separation of those acids which form with oxide of silver compounds insoluble in water, from the same cause which renders the separation of acids by chloride of barium uncertain, viz. the ammoniacal salt formed prevents the reprecipitation of several of the salts of silver by ammonia, from the acid solution. Nitrate of silver, besides effecting the separation of chlorine, iodine, bromine, cyanogen, &c., and indicating the presence of chromic acid, &c., serves, like the chloride of barium, to demonstrate at once the absence of a great many acids, where it produces no precipitate in neutral solutions.

The deportment which the solution under examination exhibits with chloride of barium and with nitrate of silver, indicates therefore at once the further course of the investigation. Thus, for instance, where chloride of barium has produced a precipitate, whilst nitrate of silver has failed to do so, it is not necessary to test for phosphoric acid, chromic acid, boracic acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, provided always the solution did not already contain salts of ammonia. The same is the case if we obtain a precipitate by nitrate of silver, but none by chloride of barium.

Returning now to the supposition which we have assumed here, viz., that the whole of the acids are present in the solution under examination, the reactions with chloride of barium and nitrate of silver would accordingly have demonstrated already the presence of SULPHURIC ACID, and led to the application of the special tests for CHLORINE, BROMINE, IODINE, CYANOGEN, FERROCYANOGEN, FERRICYANOGEN, and SULPHUR;* and there would be reason to test for all the other acids precipitable by these two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained in the course of the present work: the same remark applies to the rest of the inorganic acids, viz., nitric acid and chloric acid.

Of the organic acids, oxalic acid, paratartaric acid, and tartaric acid, are precipitated by chloride of calcium in the cold, in presence of chloride of ammonium; the two former immediately, the latter often only after some time; but the precipitation of citrate of lime is prevented by the presence of salts of ammonia, and ensues only upon ebullition or upon mixing the solution with alcohol; the latter agent serves also to effect the separation of malate of lime from aqueous solutions. If, therefore, we add to our fluid,—

3. *Chloride of Calcium* and Chloride of Ammonium,

OXALIC ACID, PARATARTARIC ACID, and TARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, phosphate of lime for instance, precipitate along with them. We must therefore select for the individual detection of the precipitated organic acids such reactions only as preclude the possibility of con-

* For the separation and special detection of these substances, I refer to § 157.

founding the organic acids with the inorganic acids that have been thrown down along with them. For the detection of oxalic acid we select accordingly solution of sulphate of lime, with acetic acid (§ 146); to effect the detection of the tartaric and paratartaric acids, we treat the precipitate produced by chloride of calcium with solution of soda, since the lime-salts of these two acids only are soluble in this menstruum in the cold, but insoluble upon ebullition.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID and MALIC ACID precipitate upon addition of alcohol to the fluid filtered from the oxalate, tartrate, &c., of lime, and which still contains an excess of chloride of calcium. Sulphate and borate of lime invariably precipitate along with the malate and citrate of lime, if sulphuric acid and boracic acid happen to be present; the analyst must therefore carefully guard against confounding the lime precipitates of these acids with those of citric acid and malic acid. The alcohol is now removed by evaporation, and,—

4. *Sesquichloride of Iron*

added. This reagent precipitates SUCCINIC ACID and BENZOIC ACID, in combination with sesquioxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several groups from each other, and the individual detection of the various acids, have been fully described and explained in the former part of this work.

B. SPECIAL REMARKS AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

To § 187.

At the commencement of § 187, the analyst is directed to mix neutral or acid aqueous solutions with hydrochloric acid. This should be done drop by drop. If no precipitate forms, a few drops are sufficient, since the only object in that case is to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group, by hydrosulphuric acid. In the case of the formation of a precipitate, some chemists recommend that a fresh portion of the solution should be acidified with nitric acid. However, even leaving the fact out of consideration that nitric acid also produces precipitates in many cases—in a solution of potassio-tartrate of antimony, for instance—I prefer the use of hydrochloric acid, *i.e.* the complete precipitation by that acid of all that is precipitable by it, for the following reasons:—1. Metals are more readily precipitated by hydrosulphuric acid from solutions acidified with hydrochloric acid, than from those acidified with nitric acid;—2. In cases where the solution contains silver, suboxide of mercury, or lead, the further analysis is materially facilitated by the total or partial precipitation of these three metals in the form of chlorides;—and 3. This latter form is the best adapted for the individual detection of these three metals when present in the same solution. Besides, the application of hydrochloric acid saves the necessity of examining whether the mercury, which may be subsequently detected with the other metals of the fifth

group, was originally present in the form of oxide or in that of suboxide. That the lead, if present in large proportion, is obtained partly in the form of a chloride, and partly in the precipitate produced by hydrosulphuric acid in the acid solution, can hardly be thought an objection to the application of this method, as the removal of the larger portion of the lead from the solution, effected at the commencement, will only serve to facilitate the examination for other metals of the fifth and sixth groups.

As already remarked, a basic salt of teroxide of antimony may separate from potassio-tartrate of antimony, for instance, or from some other analogous compound, and precipitate along with the insoluble chloride of silver and subchloride of mercury, and the sparingly soluble chloride of lead. This precipitate, however, is readily soluble in the excess of hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the fluid mixed with hydrochloric acid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated subchloride of mercury into chloride.

Should bismuth or chloride of antimony be present, the addition of the washings of the precipitate produced by hydrochloric acid to the first filtrate will cause turbidity, if the amount of free hydrochloric acid present is not sufficient to prevent the separation of the basic salt. This turbidity exercises, however, no influence upon the further process, since hydrosulphuric acid as readily converts these finely-divided precipitates into sulphides, as if the metals were in actual solution.

In the case of alkaline solutions, the addition of hydrochloric acid must be continued until the fluid shows a strongly acid reaction. The substance which causes the alkaline reaction of the fluid combines with the hydrochloric acid, and the bodies originally dissolved in that acid separate. Thus, if the alkali was present in the free state, oxide of zinc, for instance, or alumina, &c., may precipitate. But these oxides redissolve in an excess of hydrochloric acid, whereas chloride of silver would not redissolve, and chloride of lead only with difficulty. If a metallic sulphur salt was the cause of the alkaline reaction, the sulphur acid, *e. g.*, tersulphide of antimony, precipitates upon the addition of the hydrochloric acid, whilst the sulphur base, *e. g.*, sulphide of sodium, transposes with the constituents of the hydrochloric acid, forming chloride of sodium and hydrosulphuric acid. If an alkaline carbonate, a cyanide, or the sulphide of an alkali metal was the cause of the alkaline reaction, carbonic acid, hydrocyanic acid, or hydrosulphuric acid escapes. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of entire groups of bodies.

To § 188.

A judicious distribution and economy of time is especially to be studied in the practice of analysis; many of the operations may be carried on simultaneously, which the student will readily perceive and arrange for himself.

In cases where the analyst has simply to deal with metallic oxides of the sixth group—*e. g.*, teroxide of antimony—and of the fourth or fifth

group—*e. g.*, iron or bismuth—he need not precipitate the acidified solution with hydrosulphuric acid, but may, after neutralization, at once add sulphide of ammonium in excess. The sulphide of iron, &c., will in that case precipitate, whilst the antimony, &c., will remain in solution, from which they will, by addition of an acid, at once be thrown down as tersulphide of antimony, &c. This method has the advantage that the fluid is diluted less than is the case where solution of hydrosulphuric acid is employed, and that the operation is performed more expeditiously and conveniently than is the case where hydrosulphuric acid gas is conducted into the fluid. Finally, I must once more remind the student that the perfect purity of the reagents, and their application in correct quantity, rank amongst the most indispensable conditions of successful analysis. This applies more particularly to hydrosulphuric acid, especially when used in the gaseous form. In such cases, students often lose sight of the circumstance that hydrosulphuric acid gas fails to precipitate highly acid solutions unless they be previously diluted with water.

To § 191.

Besides the methods described in the systematic course to distinguish between cadmium, copper, lead, and bismuth, the following process will also be found to give highly satisfactory results. Add carbonate of soda to the nitric acid solution as long as a precipitate continues to form, then solution of cyanide of potassium in excess, and heat gently. This effects the complete separation of lead and bismuth in the form of carbonates, whilst copper and cadmium are obtained in solution in the form of cyanide of copper and potassium, and cyanide of cadmium and potassium. Lead and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in cyanide of potassium, hydrosulphuric acid in excess, gently heating, and then adding some more cyanide of potassium, in order to redissolve the sulphide of copper which may have precipitated along with the sulphide of cadmium. A residuary yellow precipitate (sulphide of cadmium), insoluble in the cyanide of potassium, demonstrates the presence of cadmium. Filter the fluid from this precipitate, and add hydrochloric acid to the filtrate, when the formation of a black precipitate (sulphide of copper) will demonstrate the presence of copper.

To § 202.

The analysis of cyanogen compounds is not very easy in certain cases, and it is sometimes a difficult task even to ascertain whether we have really a cyanide before us or not. However, if the reactions of the substance under examination upon ignition (§ 174, A, I. 2, *e* **[8]**) be carefully observed, and also whether upon boiling with hydrochloric acid any odor of hydrocyanic acid is emitted (§ 178, 2 **[34]**), the presence or absence of a cyanide will generally not long remain a matter of doubt.

It must above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two distinct classes. Viz., they are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN or some other analogous compound radical.

All the simple cyanides are decomposed by boiling with concentrated hydrochloric acid, into metallic chlorides and hydrocyanic acid. Their analysis is therefore never difficult. But the ferrocyanides, &c., to which indeed the method described § 202 more exclusively refers, suffer by acids such complicated decompositions that their analysis by means of acids is a task not so easily accomplished. Their decomposition by potassa (or soda) is far more simple. The alkali yields its oxygen to the metal combined with the ferrocyanogen, &c., the oxide thus formed precipitates, and the reduced potassium or sodium forms with the liberated radical soluble ferrocyanide, &c., of potassium (or sodium, as the case may be). But several oxides are soluble in an excess of potassa, as, *e. g.*, oxide of lead, oxide of zinc, &c. If, therefore, the double ferrocyanide of zinc and potassium, for instance, is boiled with solution of caustic potassa, it dissolves completely in that menstruum, and we may assume that the solution contains ferrocyanide of potassium, and oxide of zinc dissolved in potassa. Were we to add an acid to this solution, we should of course simply re-obtain the original precipitate of the double ferrocyanide of zinc and potassium, and the experiment would consequently be of no avail. To prevent this failure, conduct hydrosulphuric acid into the solution in potassa. This serves to convert into sulphides all the heavy metals which the potassa holds in solution as oxides. Those sulphides which are insoluble in potassa, such as sulphide of lead, sulphide of zinc, &c., precipitate, whilst those which are soluble in alkaline sulphides, such as bisulphide of tin, tersulphide of antimony, &c., remain in solution, and separate only upon the addition of an acid.

The fluid filtered from the precipitated oxides and sulphides accordingly always contains the cyanogen as ferrocyanide, &c., of potassium—provided, of course, the analyzed compound is really a double ferrocyanide, &c. From most of these compounds—ferrocyanide, ferricyanide, chromicyanide, and manganocyanide of potassium—the cyanogen partly separates as hydrocyanic acid, upon boiling the solutions with sulphuric acid, and may thus be readily detected by this means, should the direct way of detecting the radicals not succeed. But the cobalticyanide of potassium is not decomposed by sulphuric acid, and the analyst is accordingly directed to effect the detection of the compound radical in that salt by means of solution of nickel, manganese, zinc, &c. By fusion with nitrate of potassa, all these double compounds suffer decomposition, cobalticyanide of potassium not excepted. The reason why the fusion of these double compounds with nitrate of potassa should be preceded by evaporation with an excess of nitric acid, is simply to prevent the occurrence of explosions. Caution is always highly advisable in this operation.

If you simply wish to examine for certain bases in simple or compound cyanides, and for that purpose to destroy the cyanogen compound, mix the body under examination with 3 parts of sulphate and 1 part of nitrate of ammonia, and heat in a porcelain crucible under a chimney, to carry off the fumes. Complete decomposition ensues even at a moderate heat, the whole of the cyanide volatizing in form of cyanide of ammonium and products of the decomposition of the latter, whilst the metals are left behind as sulphates (*Bolley*).

APPENDIX.

I.

Deportment of the most important Medicinal Alkaloids with Reagents, and Systematic Method of effecting the Detection of these Substances.

§ 227.

The detection and separation of the vegeto-alkalies, or alkaloids, is a task of far greater difficulty than that of most of the inorganic bases. Although this difficulty is in some measure owing to the circumstance that scarcely one of the compounds which the alkaloids form with other substances is absolutely insoluble or particularly characterized by its color or any striking property, yet the principal cause of it must be ascribed to the want of accurate and minute investigations of the salts and other compounds of the alkaloids, and of the products of their decomposition. We consequently generally see and apprehend the reactions only in their external manifestation, but without being able to connect them with the causes producing them, which makes it impossible to understand all the conditions which may exercise a modifying influence.

Although therefore, in the present imperfect state of our knowledge of these bodies, an attempt to define their deportment with reagents, and base thereon a method of effecting their separation, or, at least, their individual detection in presence of each other, must of necessity fall very short of perfection, yet, having made a great many experiments on the nature and behavior of these substances, I will attempt here, for the benefit of young chemists, and more particularly pharmaceutists, to describe in some measure the reactions which the most important of the alkaloids manifest with other bodies, and to lay down a systematic method of effecting their individual detection.

The classification of the alkaloids into groups, which I have adopted, is based upon their deportment with certain general reagents. I have verified by numerous experiments the whole of the reactions described in the succeeding paragraphs.

I. Volatile Alkaloids.

The volatile alkaloids are fluid at the common temperature, and may be volatilized in the pure state as well as when mixed with water. They are accordingly obtained in the distillate when their salts are distilled with strong fixed bases and water. Their vapors, when brought in contact with those of volatile acids, form a white cloud.

1. Nicotia, or Nicotine ($C_{10}\ H_7\ N$).

§ 228.

1. Nicotia, in its pure state, forms a colorless, oily liquid, of 1·048 sp. gr.; the action of air imparts a yellowish or brownish tint to it. It boils at 482° F., suffering, however, partial decomposition in the process; but, when heated in a stream of hydrogen gas, it distils over unaltered, between 212° and 392° F. It is miscible in all proportions with water, alcohol, and ether.

Nicotia has a peculiar, disagreeable, somewhat ethereal, tobacco-like odor, an acrid, pungent taste, and very poisonous properties. Dropped on paper, it makes a transparent stain, which slowly disappears; it turns turmeric paper brown, and reddened litmus paper blue. Concentrated aqueous solution of nicotia shows these reactions more distinctly than the alkaloid in the pure state.

2. Nicotia has the character of a pretty strong base; it precipitates metallic oxides from their solutions, and forms salts with acids. The salts of nicotia are freely soluble in water and alcohol, insoluble in ether; they are inodorous, but taste strongly of tobacco; part of them are crystallizable. Their solutions, when distilled with solution of potassa, give a distillate containing nicotia. By neutralizing this with oxalic acid, and evaporating, oxalate of nicotia is produced, which may be freed from any admixture of oxalate of ammonia, by means of spirit of wine, in which the former salt is soluble, the latter insoluble.

3. If an aqueous solution of nicotia, or a solution of a salt of nicotia mixed with solution of soda or potassa, is shaken with *ether*, the nicotia is dissolved by the ether; if the latter is then allowed to evaporate on a watch-glass, the nicotia remains behind in drops and streaks; on warming the watch-glass, it volatilizes in white fumes of strong odor.

4. *Bichloride of platinum* produces in aqueous solutions of nicotia whitish-yellow, flocculent precipitates. On heating the fluid containing the precipitate, the latter dissolves, but upon continued application of heat it very speedily separates again in form of an orange-yellow, crystalline, heavy powder, which, under the microscope, appears to be composed of roundish crystalline grains. If a rather dilute solution of nicotia, supersaturated with hydrochloric acid, is mixed with bichloride of platinum, the fluid at first remains clear; after some time, however, the double salts separate in small crystals (oblique, four-sided prisms), clearly discernible with the naked eye.

5. *Terchloride of gold* produces a reddish-yellow, flocculent precipitate, sparingly soluble in hydrochloric acid.

6. Solution of *iodine in iodide of potassium* and water, when added in small quantity to an aqueous solution of nicotia, produces a yellow precipitate, which after a time disappears. Upon further addition of iodine solution, a copious, kermes-colored precipitate separates; but this also disappears again after a time.

7. Solution of *tannic acid* produces a copious, white precipitate, which redissolves upon addition of hydrochloric acid; but if a large quantity of hydrochloric acid is then added to the solution, an abundant precipitate again makes its appearance.

8. If an aqueous solution of nicotia is added to a solution of *chloride*

of mercury in excess, an abundant, flocculent, white precipitate is formed. If solution of chloride of ammonium is now added to the mixture in sufficient quantity, the entire precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy, white precipitate.

2. Conia, or Conine (C_{16} H_{15} N).

§ 229.

1. Conia forms a colorless, oily liquid, of 0·89 sp. gr.; the action of the air imparts to it a brown tint. In the pure state it boils at about 392° F.; when heated in a stream of hydrogen gas, it distils over unaltered; but when distilled in vessels containing air, it turns brown and suffers partial decomposition; with aqueous vapors it distils over freely. It dissolves sparingly in water, 100 parts of water of the common temperature dissolving 1 part of conia. The solution turns turbid on warming. Conia is miscible in all proportions with alcohol and ether. The aqueous and alcoholic solutions manifest strong alkaline reaction. Conia has a very strong, pungent, repulsive odor, which affects the head, a most acrid and disagreeable taste, and very poisonous properties.

2. Conia is a powerful base; it accordingly precipitates metallic oxides from their solutions, in a similar way to ammonia, and forms salts with acids. The salts of conia are soluble in water and in spirit of wine, but nearly insoluble in ether. The solutions of the salts turn brownish upon evaporation with partial decomposition of the conia. The dry salts of conia do not smell of the alkaloid; when moistened, they smell only feebly of it; but upon addition of solution of soda, they at once emit a strong conia odor. When salts of conia are distilled with solution of soda, the distillate contains conia. On neutralizing this with oxalic acid, evaporating to dryness, and treating the residue with spirit of wine, the oxalate of conia formed is dissolved, whilst any oxalate of ammonia that may be present is left undissolved. As conia is only sparingly soluble in water, and dissolves with still greater difficulty in solutions of alkalies, a concentrated solution of a salt of conia turns milky, upon addition of solution of soda. The minute drops which separate unite gradually, and collect on the surface.

3. If an aqueous solution of a salt of conia is shaken with solution of soda and ether, the conia is dissolved by the ether. If the latter is then allowed to evaporate in a watch-glass, the conia is left behind in yellowish-colored, oily drops.

4. *Concentrated nitric acid* imparts a fine blood-red tint to conia; *sulphuric acid*, a purple-red color, which subsequently turns to olive-yellow.

5. *Terchloride of gold* produces a yellowish-white precipitate, insoluble in hydrochloric acid; *chloride of mercury*, a copious white precipitate, soluble in hydrochloric acid. *Bichloride of platinum* does not precipitate aqueous solutions of salts of conia, the conia compound corresponding to ammonio-bichloride of platinum being insoluble in spirit of wine and ether, but soluble in water.

6. With solution of *iodine in iodide of potassium* and water, and with solution of *tannic acid*, conia comports itself the same as nicotia.

7. *Chlorine water* produces in a mixture of water and conia a strong, white turbidity.

The volatile alkaloids are easily recognised when pure; the great object of the analyst must accordingly always be to obtain them in that state. The way of effecting this is the same for nicotia as for conia, and has already been given in the foregoing paragraphs, viz., to distil with addition of solution of soda, neutralize with oxalic acid, evaporate, dissolve in alcohol, evaporate the solution, treat the residue with water, add solution of soda, shake the mixture with ether, and let the latter evaporate spontaneously. Conia is distinguished from nicotia chiefly by its odor, its sparing solubility in water, and its comportment with chlorine.

II. Non-volatile Alkaloids.

The non-volatile alkaloids are solid, and cannot be distilled over with water.

First Group.

Non-volatile Alkaloids which are precipitated by Potassa or Soda from the Solutions of their Salts, and redissolve readily in an Excess of the Precipitant.

Of the alkaloids of which I purpose to treat here, *one* only belongs to this group, viz.,

Morphia, or Morphine ($C_{34} H_{19} N O_6 = \overset{+}{Mo}$).

§ 230.

1. Crystallized morphia ($\overset{+}{Mo} + 2$ aq.) usually appears in the form of colorless, brilliant, four-sided prisms, or, when obtained by precipitation, as a white crystalline powder. It has a bitter taste, and dissolves very sparingly in cold, but somewhat more readily in boiling water. Of cold alcohol it requires about 90 parts by weight for solution; of boiling alcohol from 20 to 30 parts. The solutions of morphia in alcohol as well as in hot water manifest distinctly alkaline reaction. This alkaloid is nearly insoluble in ether. At a moderate heat the crystallized morphia loses the two equivalents of water.

2. Morphia neutralizes acids completely, and forms with them the salts of morphia. These salts are readily soluble in water, and in spirit of wine, but insoluble in ether; their taste is disagreeably bitter. Most of them are crystallizable.

3. *Potassa* and *ammonia* precipitate from the solutions of salts of morphia—generally only after some time—$\overset{+}{Mo} + 2$ aq., in the form of a white crystalline powder. Stirring and friction on the sides of the vessel promote the separation of the precipitate, which redissolves with great readiness in an excess of potassa, but more difficultly in ammonia. It dissolves also in chloride of ammonium and, though with difficulty only, in carbonate of ammonia.

4. *Carbonate of potassa and carbonate of soda* produce the same precipitate as potassa and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkaline bicarbonate is added to a solution of morphia in caustic potassa, or if carbonic acid is conducted

into the soution, $\overset{+}{Mo} + 2$ aq. separates,—especially after previous ebullition—in the form of a crystalline powder. A more minute inspection, particularly through a magnifying-glass, shows this powder to consist of small acicular crystals; seen through a glass which magnifies 100 times, these crystals present the form of four-sided prisms.

5. *Bicarbonate of soda and bicarbonate of potassa* speedily produce in solutions of neutral salts of morphia a precipitate of hydrated morphia, in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of salts of morphia in the cold.

6. The action of strong *nitric acid* upon morphia or one of its salts, in the solid state or in concentrated solutions, produces a fluid varying from red to yellowish-red. Dilute solutions do not change their color upon addition of nitric acid in the cold, but upon heating they acquire a yellow tint.

7. *Neutral sesquichloride of iron* imparts to neutral solutions of salts of morphia a beautiful dark blue color, which disappears upon the addition of an acid. If the solution contains an admixture of animal or vegetable extractive matters, or of acetates, the color will appear clouded and less distinct.

8. If *iodic acid* is added to a solution of morphia or of a salt of morphia, IODINE separates. In concentrated aqueous solutions the separated iodine appears as a kermes-brown precipitate, whilst to alcoholic and dilute aqueous solutions it imparts a brown or yellowish-brown color. The addition of starch-paste to the fluid, no matter whether made before or after that of the iodic acid, considerably heightens the delicacy of the reaction, since the blue tint of the iodide of starch remains still perceptible in exceedingly dilute solutions, which is not the case with the brown color imparted by iodine. As other nitrogenous bodies (albumen, caseine, fibrine, &c.) likewise reduce iodic acid, this reaction has only a relative value.

SECOND GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY BICARBONATE OF SODA EVEN FROM ACID SOLUTIONS, if the latter are not diluted in a larger proportion than 1 : 100; Narcotina, Quina, Cinchonia.

a. NARCOTINA, OR NARCOTINE ($C_{46}H_{25}NO_{14} = \overset{+}{Na}$).

§ 231.

1. Crystallized narcotina ($\overset{+}{Na}$ + aq.) appears usually in the form of colorless, brilliant, straight rhombic prisms, or, when precipitated by alkalies, as a white, loose, crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but somewhat more readily upon heating. Solid narcotina is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotina does not alter vegetable colors. At 338° F. it fuses, with loss of 1 eq. of water.

2. Narcotina dissolves readily in acids, combining with them to salts.

These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even upon simple evaporation. Most of the salts of narcotina are amorphous, and soluble in water, alcohol, and ether; they have a bitter taste.

3. *Pure alkalies*, and *alkaline carbonates* and *bicarbonates*, immediately precipitate from the solutions of salts of narcotine ($\overset{+}{Na}$ + aq.) in the form of a white powder, which, seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitants. If a solution of narcotina is mixed with ammonia, and ether added in sufficient quantity, the narcotina which has separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the ethereal solution is evaporated in a watch-glass, the residue is seen, upon inspection through a lens magnifying 100 times, to consist of small, distinct, elongated, and lance-shaped crystals.

4. *Concentrated nitric acid* dissolves narcotina to a colorless fluid, which acquires a pure yellow tint upon application of heat.

5. *Concentrated sulphuric acid* dissolves narcotina to a yellow fluid, which turns brown upon application of heat. A solution of narcotina in concentrated sulphuric acid containing a *slight* admixture of nitric acid, appears of an intense blood-red color, which disappears altogether upon the addition of a somewhat larger amount of nitric acid.

6. If the solution of a salt of narcotina is mixed with *chlorine water*, it acquires a yellow color, slightly inclining to green; if ammonia is then added, a much more intensely colored, yellowish-red fluid is obtained.

7. If narcotina or one of its salts is dissolved in an excess of dilute *sulphuric acid*, some finely levigated *binoxide of manganese* added, the mixture heated to boiling, and kept in ebullition for the space of several minutes, the narcotina absorbs oxygen and is converted into opianic acid, cotarnine (a base soluble in water), and carbonic acid. Ammonia will now of course fail to precipitate narcotina from the filtrate.

b. Quina, or Quinine ($C_{40}H_{24}N_2O_4 = \overset{+}{Q}$).

§ 232.

1. Crystallized quina ($\overset{+}{Q}$ + 2 aq.) appears either in the form of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble in cold, but somewhat more readily in hot water. It is readily soluble in spirit of wine, both cold and hot, but less so in ether. The taste of quina is intensely bitter; the solutions of quina manifest alkaline reaction. Upon exposure to heat it loses the 2 eq. of water.

2. Quina neutralizes acids completely. The salts taste intensely bitter; most of them are crystallizable, and for the greater part readily soluble in water and in spirit of wine. Acid solutions reflect a bluish tint.

3. *Potassa*, *ammonia*, and the neutral *carbonates of the alkalies*, produce in solutions of salts of quina (if they are not too dilute) a white,

loose, pulverulent precipitate of hydrated quina, which immediately after precipitation appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of an aggregate of crystalline needles. The precipitate redissolves only to a scarcely perceptible extent in an excess of potassa, but more readily in ammonia. It is hardly more soluble in fixed alkaline carbonates than in pure water. If a solution of quina is mixed with ammonia, ether added, and the mixture shaken, the quina which has separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. In this point quina differs essentially from cinchonia; by means of this reaction the former may therefore be readily detected in presence of the latter, and separated from it.

4. *Bicarbonate of soda* also produces both in neutral and acid solutions of salts of quina a white precipitate. In acidified solutions containing 1 part of quina to 100 parts of acid and water, the precipitate forms immediately;—if the proportion of the quina to the acid and water is as 1 : 150, the precipitate separates only after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is as 1 : 200, the fluid remains clear, and it is only after from twelve to twenty-four hours' standing that a slight precipitate makes its appearance. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more complete, the less the excess of the precipitant; the precipitate contains carbonic acid.

5. *Concentrated nitric acid* dissolves quina to a colorless fluid, turning yellowish upon application of heat.

6. The addition of *chlorine water* to the solution of a salt of quina fails to impart a color to the fluid, or, at least, imparts to it only a very faint tint; but if ammonia is now added the fluid acquires an intensely emerald-green color. If, after the addition of the chlorine water some solution of *ferrocyanide of potassium* is added, and after this a few drops of ammonia or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. This reaction is delicate and characteristic. Upon addition of an acid* to the red fluid, the color vanishes, but reappears afterwards upon cautious addition of ammonia. (*O. Livonius*' Letters; *A. Vogel.*)

7. *Concentrated sulphuric acid* likewise dissolves pure quina and pure salts of quina to a colorless fluid, which does not acquire any coloration upon being heated to the point of incipient evaporation of the sulphuric acid, but turns afterwards yellow, and finally brown. Sulphuric acid containing an admixture of nitric acid dissolves quina to a colorless or very faint yellowish fluid.

c. Cinchonia, or Cinchonine ($C_{40}H_{24}N_2O_2 = \overset{+}{Ci}$).

§ 233.

1. Cinchonia appears either in the form of transparent, brilliant, four-sided prisms, or fine white crystalline needles, or, when precipitated from concentrated solutions, as a loose white powder. At first it appears tasteless, but after some time the bitter taste of the bark becomes perceptible. It is nearly insoluble in cold water, and dissolves only with

* Acetic acid answers the purpose best.

exceeding difficulty in hot water; it dissolves sparingly in cold dilute spirit of wine, more readily in hot spirit of wine, and the most freely in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonia separates upon cooling in a crystalline form. Solutions of cinchonia taste bitter, and manifest alkaline reaction. Cinchonia is insoluble in ether.*

2, Cinchonia neutralizes acids completely. The salts have the bitter taste of the bark; most of them are crystallizable; they are generally more readily soluble in water and in spirit of wine than the corresponding quina compounds. Ether fails to dissolve them.

3. Cinchonia, when heated cautiously, fuses at first without loss of water; subsequently white fumes arise which, like benzoic acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odor being exhaled at the same time. If the operation is conducted in a stream of hydrogen gas, long, brilliant prisms are obtained (*Hlasiwetz*).

4. *Potassa, ammonia,* and the *neutral carbonates of the alkalies* produce in solutions of salts of cinchonia a white, loose precipitate of CINCHONIA, which does not redissolve in an excess of the precipitants. If the solution was concentrated, the precipitate does not exhibit a distinctly crystalline appearance, even though viewed through a lens magnifying 200 times; but if the solution was so dilute that the precipitate formed only after some time, it appears under the microscope to consist of distinct crystalline needles aggregated into star-shaped tufts.

5. *Bicarbonate of soda* and *bicarbonate of potassa* precipitate cinchonia in the same form as in 4, both from neutral and acid solutions, but not so completely as the simple carbonates of the alkalies. In solutions containing 1 part of cinchonia to 200 parts of water and acid, the precipitate still forms immediately; its quantity increases after standing some time.

6. *Concentrated sulphuric acid* dissolves cinchonia to a colorless fluid, which upon application of heat first acquires a brown, and finally a black color. Addition of some nitric acid leaves the solution colorless in the cold, but upon application of heat the fluid, after passing through the intermediate tints of yellowish-brown and brown, turns finally black.

7. The addition of *chlorine water* to the solution of a salt of cinchonia fails to impart a color to the fluid; if ammonia is now added, a yellowish-white precipitate is formed.

Recapitulation and Remarks.

§ 234.

The alkaloids of the second group are altered or precipitated by various other reagents besides those mentioned above; the reactions are, however, not adapted to effect their individual detection and separation. Thus, for instance, bichloride of platinum produces in solutions of the salts of the three alkaloids belonging to this group, a yellowish-

* The cinchonia of commerce usually contains in admixture another alkaloid, called cinchotina, which is soluble in ether. This alkaloid crystallizes in large rhomboidal crystals of brilliant lustre, which fuse at a high temperature, and cannot be sublimed, even in a stream of hydrogen gas (*Hlasiwetz*).

white precipitate, chloride of mercury a white precipitate, tincture of galls a yellowish-white, flocculent precipitate, &c.

Narcotina and quina being soluble in ether, whilst cinchonia is insoluble in that menstruum, the former may be most readily separated by this means from the latter alkaloid. For this purpose the analyst need simply mix the solution of the three alkaloids with ammonia in excess, then add ether, and separate the solution of quina and narcotine from the undissolved cinchonia. If the ethereal solution is now evaporated, the residue dissolved in hydrochloric acid and a sufficient amount of water to make the dilution as 1 : 200, and bicarbonate of soda is then added, the narcotina precipitates, whilst the quina remains in solution. By evaporating the solution, and treating the residue with water, the quina is obtained in the free state.

THIRD GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, AND DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT; BUT ARE NOT PRECIPITATED FROM (even somewhat concentrated) ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALIES: Strychnia, Brucia, Veratria.

a. STRYCHNIA, OR STRYCHNINE ($C_{44}H_{24}N_2O_4 = \overset{+}{Sr}$).

§ 235.

1. Strychnia appears either in the form of white, brilliant rhombic prisms, or, when produced by precipitation or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is nearly insoluble in cold, and barely soluble in hot water. It is insoluble in absolute alcohol and ether, and difficultly soluble in dilute spirit of wine. It does not fuse when heated. It is exceedingly poisonous.

2. Strychnia neutralizes acids completely. The salts of strychnia are, for the most part, crystallizable; they are soluble in water. All the salts of strychnia have an intolerably bitter taste and are exceedingly poisonous.

3. *Potassa* and *carbonate of soda* produce in solutions of salts of strychnia white precipitates of strychnia, which are insoluble in an excess of the precipitants. Viewed through a lens magnifying one hundred times the precipitate appears as an aggregate of small crystalline needles. From dilute solutions the strychnia separates only after the lapse of some time, in the form of crystalline needles, which are distinctly visible even with the naked eye.

4. *Ammonia* produces the same precipitate as potassa. The precipitate redissolves in an excess of ammonia, but after a short time—or if the solution is highly dilute, after a more considerable lapse of time—the strychnia crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible with the naked eye.

5. *Bicarbonate of soda* produces in neutral solution of salts of strychnia a precipitate of strychnia, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline) the precipitate dissolves readily in the liberated carbonic acid.

The addition of bicarbonate of soda to an acid solution of strychnia causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnia crystallizes from the fluid in distinct prisms, in proportion as the free carbonic acid escapes. If a concentrated solution of strychnia, supersaturated with bicarbonate of soda, is boiled for some time, a precipitate forms immediately; from dilute solutions this precipitate separates only after concentration.

6. *Sulphocyanide of potassium* produces in concentrated solution of salts of strychnia immediately, and in dilute solutions after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, truncated or pointed at an acute angle, and is but little soluble in an excess of the precipitant.

7. On putting a drop of concentrated *sulphuric acid* in a watch-glass, and adding to it some strychnia or a little of a salt of strychnia, solution ensues without any particular reaction; but if a drop of solution of chromate of potassa is now added to the fluid, the latter instantly acquires a deep blue color, which speedily changes to red (*Otto*). If the strychnia is rubbed together with binoxide of lead and concentrated sulphuric acid containing 1 per cent. of nitric acid, the mass acquires first a blue, then a violet color, which changes to red, and, finally, to greenish-yellow (*E. Marchand*). The former reaction (*Otto's*) loses in distinctness, or even altogether fails to manifest itself, if the substance contains admixtures of some other organic compounds, *e. g.*, quina, sugar (*Brieger*). But by the second method (*Marchand's*) strychnia may be clearly detected even when mixed with much sugar. Ferricyanide of potassium also will produce the same reaction (*W. Davy*); with this oxidizing agent the change from violet to red and yellow takes place more slowly.

8. *Chloride of mercury* produces in solutions of salts of strychnia a white precipitate, which changes after some time to crystalline needles aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution the double compound recrystallizes in distinct needles.

9. Strong *chlorine water* produces in solution of salts of strychnia a white precipitate, which dissolves in ammonia to a colorless fluid.

10. *Concentrated nitric acid* dissolves strychnia and its salts to a colorless fluid, which becomes yellow upon the application of heat.

b. Brucia, or Brucine ($C_{46}H_{26}N_2O_8 = \overset{+}{Br}$).

§ 236.

1. Crystallized brucia ($\overset{+}{Br} + 7$ aq.) appears either in the form of transparent, straight rhombic prisms, or in that of crystalline needles aggregated into stars, or as a white powder composed of minute crystalline scales. Brucia is difficultly soluble in cold, but somewhat more readily in hot water. Both absolute and dilute alcohol dissolve it freely, but it is insoluble in ether. Its taste is intensely bitter. When heated, it fuses with loss of its water of crystallization.

2. Brucia neutralizes acids completely. The salts of brucia are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potassa* and *carbonate of soda* throw down from solutions of salts

of brucia a white precipitate of brucia, which is insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, it appears to consist of very minute grains; but, upon further inspection, these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces a whitish precipitate in solutions of salts of brucia, which appears at first like a number of minute drops of oil, but changes subsequently—with absorption of water—to small needles. The precipitate redissolves, immediately after separation, very readily in an excess of the precipitant, but after a very short time—or, in dilute solutions, after a more considerable lapse of time—the brucia, combined with crystallization water, crystallizes from the ammoniacal fluid in small concentrically grouped needles, which addition of ammonia fails to redissolve.

5. *Bicarbonate of soda* produces in neutral solutions of salts of brucia a precipitate of brucia, combined with crystallization water; this precipitate separates after the lapse of a short time, in form of concentrically aggregated needles of silky lustre, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare strychnia). Bicarbonate of soda fails to precipitate acid solutions of salts of brucia; and it is only after the lapse of a considerable time that the alkaloid separates from the fluid in regular and comparatively large crystals, in proportion as the carbonic acid escapes.

6. *Concentrated nitric acid* dissolves brucia and its salts to intensely red fluids, which subsequently acquire a yellowish-red tint, and turn completely yellow upon application of heat. Upon addition of protochloride of tin or sulphide of ammonium to the fluid heated to this point, no matter whether concentrated or after dilution with water, the faint yellow color changes to a most intense violet.

7. Addition of *chlorine water* to the solution of a salt of brucia imparts to the fluid a fine bright red tint; if ammonia is then added, the red color changes to yellowish-brown.

8. *Concentrated sulphuric acid* dissolves brucia to a faint rose-colored fluid.

9. *Sulphocyanide of potassium* produces in concentrated solutions of salts of brucia immediately, and in dilute solutions after some time, a granular crystalline precipitate, which, when viewed under the microscope, appears composed of variously aggregated polyhedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Chloride of mercury* also produces a white granular precipitate, which, when viewed under the microscope, appears composed of small round crystalline grains.

c. Veratria, or Veratrine ($C_{34}H_{22}NO_6$) $\overset{+}{Ve}$.

§ 237.

1. Veratria appears generally as a pure white, yellowish or greenish-white powder, of acrid and burning, but not bitter taste; it is exceedingly poisonous. Veratria acts with great energy upon the mem-

branes of the nose; even the most minute quantity of the powder excites the most violent sneezing. It is insoluble in water; in alcohol it dissolves readily, but more sparingly in ether. At a gentle heat it fuses like wax, and solidifies upon cooling to a transparent yellow mass.

2. Veratria neutralizes acids completely. Some salts of veratria are crystallizable, others dry up to a gummy mass. They are soluble in water, and of acrid and burning taste.

3. *Potassia, ammonia,* and the *simple carbonates of the alkalies* produce in solutions of salts of veratria a flocculent, white precipitate, which, viewed under the microscope, immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and small scattered clusters of short prismatic crystals are observed, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potassa, and of carbonate of potassa. It is slightly soluble in ammonia, in the cold, but the dissolved portion separates again upon application of heat.

4. With *bicarbonate of soda* and *bicarbonate of potassa* the salts of veratria comport themselves like those of strychnia and brucia. However, upon boiling, the veratria separates readily, even from dilute solutions.

5. If veratria is acted upon with *concentrated nitric acid,* it agglutinates into small resinous lumps, which afterwards dissolve slowly in the acid. The solution presents a faint reddish-yellow color.

6. If veratria is treated with *concentrated sulphuric acid,* it also agglutinates at first into small resinous lumps; but these dissolve with great readiness to a pale yellow fluid, the color of which gradually increases in depth and intensity, and changes afterwards to a reddish-yellow, then to an intense blood-red, subsequently to crimson, and finally to violet.

7. *Sulphocyanide of potassium* produces only in concentrated solutions of salts of veratria flocculent-gelatinous precipitates.

8. Addition of *chlorine-water* to the solution of a salt of veratria imparts to the fluid a yellowish tint, which, upon addition of ammonia, changes to a faint brownish color. In concentrated solutions chlorine produces a white precipitate.

Recapitulations and Remarks.

§ 238.

The alkaloids of the third group also are precipitated by many other reagents besides those above-mentioned, as, for instance, by tincture of galls, bichloride of platinum, &c. But as these reactions are common to all, they are of little importance in an analytical point of view.

Strychnia may be separated from brucia and veratria by means of absolute alcohol, since it is insoluble in that menstruum, whilst the two latter alkaloids readily dissolve in it. The identity of strychnia is best established by the reaction with sulphuric acid and chromate of potassa, or with binoxide of lead or ferricyanide of potassium; also by the form of its crystals—when thrown down by alkalies—viewed under the microscope; and lastly, by the form of the precipitate which sulphocyanide of potassium and chloride of mercury produce in solutions of its salts.

Brucia and veratria are not readily separated from one another, but may be detected in presence of each other. The identity of brucia is best established by the reactions with nitric acid and protochloride of tin or sulphide of ammonium, or by the form of the precipitate which ammonia produces in solutions of salts of brucia. Veratria is sufficiently distinguished from brucia and the other alkaloids which we have treated of, by its characteristic deportment at a gentle heat, and also by the form of the precipitate which alkalies produce in solutions of its salts. To distinguish veratria in presence of brucia, the reaction with concentrated sulphuric acid is employed.

To these alkaloids I will add *salicine*, although this substance does not properly belong to the same class of chemical compounds.

§ 239.

Salicine ($C_{26} H_{18} O_{14}$).

1. Salicine appears either in the form of white crystalline needles and scales of silky lustre, or, when the crystals are very small, as a powder of silky lustre. It has a bitter taste, is readily soluble in water and in alcohol, but insoluble in ether.

2. No reagent precipitates salicine as such.

3. If salicine is treated with *concentrated sulphuric acid*, it agglutinates into a resinous lump, and acquires an intensely blood-red color, without dissolving in the acid; the color of the sulphuric acid is at first unaltered.

4. If an aqueous solution of salicine is mixed with *hydrochloric acid* or *dilute sulphuric acid*, and the mixture boiled for a short time, the fluid suddenly becomes turbid, and deposits a finely granular crystalline precipitate (saliretine).

Systematic Course for the Detection of the Alkaloids treated of in the preceding Paragraphs, and of Salicine.

§ 240.

The analytical course which I am now about to describe is based upon the supposition that the analyst has to examine a concentrated aqueous solution—effected by the agency of an acid—of one or several of the non-volatile alkaloids, which solution is free from any admixture of substances that might tend to obscure or modify the reactions. For the modifications which the presence of coloring or extractive matters, &c., requires, I refer to § 243.

I. Detection of the Alkaloids, and of Salicine, in Solutions supposed to contain only one of these Substances.

§ 241.

1. Add dilute solution of potassa or soda drop by drop to a portion of the aqueous solution, until the fluid acquires a scarcely perceptible alkaline reaction; stir, and let the fluid stand for some time.

a. No precipitate is formed; this proves the total absence of the alkaloids, and indicates the presence of salicine. To set all doubt at

rest, test the original substance with concentrated sulphuric acid, and also with hydrochloric acid. Compare § 239.

b. A PRECIPITATE IS FORMED. Add solution of potassa or soda, drop by drop, until the fluid manifests a strongly alkaline reaction.

a. The precipitate redissolves : MORPHIA. To arrive at a positive conclusion on this point, test another portion of the solution with iodic acid (§ 230, 8), and a portion of the original substance with nitric acid (§ 230, 6).

β. The precipitate remains undissolved : Presence of an alkaloid of the second or third group. Pass on to 2.

2. Add to a second portion of the original solution two or three drops of dilute sulphuric acid, and then a saturated solution of bicarbonate of soda until the acid reaction is just neutralized; vigorously rub the inside of the vessel, and allow the mixture to stand for half an hour.

a. NO PRECIPITATE IS FORMED : Absence of narcotina and cinchonia. Pass on to 3.

b. A PRECIPITATE IS FORMED : Narcotina, cinchonia, and perhaps also quina, as the precipitation of the latter substance by bicarbonate of soda depends entirely upon the degree of dilution of the fluid. Add to a portion of the original solution ammonia in excess, then a sufficient quantity of ether, and shake the mixture.

a. The precipitate which forms at first upon the addition of the ammonia redissolves in the ether, and the clear fluid presents two distinct layers : narcotina or quina. To distinguish between the two, test a fresh portion of the original solution with chlorine water and ammonia. If the solution turns green, QUINA, if yellowish-red, NARCOTINA is present.

β. The precipitate which forms upon the addition of ammonia does not redissolve in the ether : CINCHONIA. The deportment of cinchonia at a high temperature may serve as a conclusive test (§ 233, 3).

3. Put a portion of the original substance, or of the residue remaining upon the evaporation of the solution, in a watch-glass, and treat with concentrated sulphuric acid.

a. A rose-colored solution is obtained, which becomes intensely red upon addition of nitric acid : BRUCIA. The reaction with nitric acid and protochloride of tin is resorted to as a conclusive test (§ 236, 6).

b. A yellow solution is obtained, the color of which gradually changes to yellowish-red, then to blood-red, and turns finally crimson : VERATRIA.

c. A colorless fluid is obtained, which remains colorless after standing for some time.

Add to the fluid a drop of chromate of potassa; if this imparts to it a deep blue color, STRYCHNIA is present; if it leaves the fluid unaltered, QUINA is present. The reaction with chlorine water and ammonia is resorted to as a conclusive test.

II. DETECTION OF THE ALKALOIDS, AND OF SALICINE, IN SOLUTIONS SUPPOSED TO CONTAIN SEVERAL OR ALL OF THESE SUBSTANCES.

§ 242.

1. Add to a portion of the aqueous solution dilute solution of potassa or soda, drop by drop, until the fluid acquires a scarcely perceptible alkaline reaction; stir, and let the fluid stand for some time.

a. NO PRECIPITATE IS FORMED; this proves the total absence of the

alkaloids, and indicates the presence of SALICINE. To remove all doubt on the point, test the original substance with concentrated sulphuric acid, and with hydrochloric acid. Compare § 241, 1, *a*.

b. A PRECIPITATE IS FORMED : add solution of potassa or soda, drop by drop, until the fluid manifests a strongly alkaline reaction.

α. *The precipitate redissolves.* Absence of the alkaloids of the second and third group. Presence of MORPHIA is indicated. The reactions with iodic acid (§ 230, 8), and with nitric acid (§ 230, 6), are resorted to as conclusive tests. Examination for salicine, see 4.

β. *The precipitate does not redissolve, or at least not completely.* Filter, and treat the precipitate as directed in 2. Saturate the filtrate with carbonic acid, or mix it with bicarbonate of soda or bicarbonate of potassa, and boil nearly to dryness. Treat the residue with water; if it dissolves completely, this is a sign that no morphia is present; but if there is an insoluble residue left, this indicates the presence of morphia. The reactions with iodic acid (§ 230, 8), and with nitric acid (§ 230, 6), are resorted to as conclusive tests.

2. Wash the filtered precipitate of 1, *b*, *β*, with cold water, dissolve in a slight excess of dilute sulphuric acid, and add solution of bicarbonate of soda to the fluid until the acid reaction is neutralized; stir the mixture, vigorously rubbing the sides of the vessel, and allow the fluid to stand for an hour.

a. NO PRECIPITATE IS FORMED. Absence of narcotina and cinchonia. Boil the solution nearly to dryness, and treat the residue with cold water. If it dissolves completely, pass on to 4; but if an insoluble residue is left, examine this for quina—of which a minute quantity might be present—and for strychnia, brucia, and veratria, according to the directions of 3.

b. A PRECIPITATE IS FORMED. This may contain narcotina, cinchonia, and also quina, compare § 241, 2, *b*. Filter, and treat the filtrate as directed § 242, 2, *a*. Wash the precipitate with cold water, dissolve in a little hydrochloric acid, add ammonia in excess, and then a sufficient quantity of ether.

α. *The precipitate which forms at first upon the addition of the ammonia redissolves completely in the ether, and the clear fluid presents two distinct layers.* Absence of cinchonia; presence of quina or narcotina. Evaporate the ethereal solution, dissolve the residue in a little hydrochloric acid and a sufficient amount of water to make the dilution at least as 1 : 200; add bicarbonate of soda to neutralization, and allow the fluid to stand for some time. The formation of a precipitate indicates the presence of NARCOTINA. Filter, and test the precipitate with chlorine water and ammonia (§ 231, 6). Evaporate the filtrate, or the fluid if no precipitate has been formed, to dryness, and treat the residue with water. If part of it remains undissolved, wash this, dissolve in hydrochloric acid, and add chlorine water and ammonia. Green color : QUINA.

β. *The precipitate produced by the ammonia does not redissolve in the ether, or at least not completely :* CINCHONIA. Quina or narcotina may also be present. Filter, and examine the filtrate for quina and narcotina as in *α*. The precipitate consists of cinchonia, and may be further examined according to § 233, 3.

3. Wash the insoluble residue of § 242, 2, *a*, with water, dry on the water-bath, and digest with absolute alcohol.

a. IT DISSOLVES COMPLETELY : absence of strychnia ; presence of (quina) brucia or veratria. Evaporate the alcoholic solution on the water-bath to dryness, and, if quina has already been detected, divide the residue into two portions, and test one part for BRUCIA, with nitric acid and protochloride of tin (§ 236, 6), and the other for VERATRIA, by means of concentrated sulphuric acid (§ 237, 6) ; but if no quina has as yet been detected, divide the residue into three portions, *a*, *b*, and *c* ; examine *a* and *b* for BRUCIA and VERATRIA, in the manner just stated, and *c* for quina, with chlorine-water and ammonia. However, if brucia is present, dissolve *c* in hydrochloric acid, add ammonia and ether, let the mixture stand for some time, evaporate the ethereal solution, and examine the residue for quina.

b. It does not dissolve, or at least not completely : presence of STRYCHNIA ; perhaps also of (quina) brucia and veratria. Filter, and examine the filtrate for (QUINA) BRUCIA and VERATRIA as directed § 242, 3, *a*. The identity of the precipitate with strychnia is demonstrated by the reaction with sulphuric acid and chromate of potassa (§ 235, 7).

4. Mix a portion of the original solution with hydrochloric acid, and boil the mixture for some time. The formation of a precipitate indicates the presence of SALICINE. To set all doubt on this point at rest, test the original substance with concentrated sulphuric acid (§ 239, 3).

DETECTION OF THE ALKALOIDS, IN PRESENCE OF COLORING AND EXTRACTIVE VEGETABLE OR ANIMAL MATTERS.

§ 243.

The presence of mucilaginous, extractive, and coloring matters renders the detection of the alkaloids a task of considerable difficulty. These matters obscure the reactions so much that we are even unable to determine by a preliminary experiment, whether the substance under examination contains one of the alkaloids we have treated of in the foregoing paragraphs, or not. I will now give several methods by means of which the separation of the alkaloids from such extraneous matters may be effected, and their detection be made practicable. Which of these methods to select will, of course, always depend upon the particular circumstances of the case.

1. STAS'S METHOD FOR EFFECTING THE DETECTION OF POISONOUS ALKALOIDS.*

a. If you have to look for the suspected organic bases in the contents of the stomach or intestines, or in articles of food, or in pulpy matters in general, heat the suspected substance with double its weight of strong alcohol, acidified with from 0·5 grm. to 2 grm. of tartaric acid or oxalic acid, to from 158° F. to 167° F. When quite cold, filter, and wash the undissolved part with strong alcohol, adding the washings to the filtrate.

If you have to deal with the heart, liver, lungs, or similar organs, cut them into fine shreds, moisten with the acidified alcohol, press, and repeat the same operation, until the soluble parts are completely extracted ; collect the fluids obtained, and filter.

* "Bulletin de l'Académie de Médecine de Belgique," IX. 304. "Jahrb. f. prakt. Pharm.," XXIV. 313. "Jahresbericht" von *Liebig* und *Kopp*, 1851, p. 640.

b. Concentrate the alcoholic fluid at a temperature not exceeding 95° F., and, if no insoluble matter separates, continue to evaporate nearly to dryness. Conduct this process, either under a bell-glass over sulphuric acid, with or without rarefaction of the air, or in a tubular retort, through which a current of air is passed. If fatty or other insoluble matters separate in the process of concentration, pass the concentrated fluid through a moistened filter, and evaporate the filtrate nearly to dryness, conducting the process, as above, either under a bell-glass or in a retort.

c. Digest the residue with cold absolute alcohol, filter, wash the insoluble residue thoroughly with alcohol, and let the alcoholic solution evaporate in the air or in vacuo; dissolve the acid residue in a little water, and add bicarbonate of soda as long as effervescence ensues.

d. Add to the mixture four or five times its volume of ether, and shake; then allow it to stand at rest; let a little of the supernatant ether evaporate spontaneously in a watch-glass. If this leaves oily streaks upon the glass, which gradually collect into a drop, and emit, upon the application of a gentle heat, a disagreeable, pungent, and stifling odor, there is reason to infer the presence of a liquid volatile base; whilst a solid residue or a turbid fluid, with solid particles suspended in it, indicates a non-volatile, solid base. In the latter case, the base may emit a disagreeable animal smell, but not a pungent odor, as with volatile bases. The blue color of reddened litmus paper is permanently restored. If no residue is left, add to the fluid some solution of soda or potassa, and shake with repeatedly renewed ether, which will now dissolve the base. It follows from the assumption that the bases present will pass into the ethereal solution, that *Stas's* method is principally calculated for the detection of the poisonous alkaloids which are soluble in ether, though some of them only difficultly. The following are the vegeto-alkalies which *Stas* enumerates as discoverable by his method: Conia, Nicotina, Aniline, Picoline, Petinine, Morphia, Codeia, Brucia, Strychnia, Veratria, Colchicia, Delphia, Emetine, Solania, Aconita, Atropia, and Hyoscyamia.

a. There is reason to infer the presence of a volatile base.

Add to the contents of the vessel from which you have taken the small portion of ether for evaporation in the watch-glass, one or two cubic centimetres of strong solution of potassa or soda, shake the mixture, let it stand at rest, pour the supernatant fluid into a flask, and treat the residue again three or four times with ether, until the last portion poured off leaves no longer a residue upon evaporation. Mix the ethereal fluid with some dilute sulphuric acid until the well-shaken fluid manifests acid reaction; allow the mixture to stand at rest, decant the supernatant ether from the acid aqueous fluid, and treat the latter once more with ether in the same way.

aa. Mix the residual acid solution (which may contain sulphates of ammonia, nicotina, aniline, picoline, and petinine, indeed which must contain these bases, if they are present in the examined substances, since their compounds with sulphuric acid are quite insoluble in ether; and in which, if conia is present, the greater part of the latter alkaloid is also found) with concentrated solution of soda or potassa in excess, and treat with ether, which will again dissolve the liberated bases; decant the ether, and leave it to spontaneous evaporation, at the lowest possible temperature; place the dish with the residue in vacuo over sulphuric acid. In this process

the ether and ammonia escape, leaving the volatile organic base behind in the pure state. The nature of the organic base is then finally ascertained.

bb. The ether decanted from the acid solution contains the animal matters which it has removed from the alkaline fluid. It leaves therefore, upon spontaneous evaporation, a trifling, faint yellow residue of nauseous odor, which contains also some sulphate of conia, if that base was present in the examined matter.

β. There is reason to infer the presence of a solid base.

Add a few drops of alcohol to the ethereal solution obtained by treating with ether the previously acid residues mixed either simply with bicarbonate of soda, or first with that reagent and then with solution of soda or potassa (see *c* and *d*), and leave the mixture to spontaneous evaporation. If this fails to give the base in a distinctly crystalline form and sufficiently pure, add a few drops of water feebly acidified with sulphuric acid, which will usually serve to separate the mass into a fatty portion, adhering to the dish, and an acid aqueous solution, which contains the base as a bisulphate. Decant or filter, wash with a little slightly acidified water, and evaporate the solution to a considerable extent, under a bell-glass over sulphuric acid. Mix the residue with a highly concentrated solution of pure carbonate of potassa, treat the mixture with absolute alcohol, decant, and let the alcoholic fluid evaporate, which will generally leave the base behind in a state of perfect purity or nearly so.

This method, which gives very satisfactory results with alkaloids soluble in ether, and especially with volatile alkaloids, may lead to mistakes in the case of those alkaloids which are insoluble or only sparingly soluble in ether, as, *e. g.*, morphia, the solution of which in caustic alkalies, when shaken with ether, will hardly yield any of the alkaloid to the latter fluid. Never neglect, therefore, to mix the alkaline fluid obtained in *d*—after repeated extraction with ether, and subsequent addition of some more solution of soda, to dissolve the morphia, which may have separated, and after evaporation of the ether still present—with a concentrated solution of chloride of ammonium, and let the mixture stand in the open air. If morphia is present, it will separate in the form of crystals.*

2. Merck's Method of effecting the Detection of all Non-volatile Alkaloids.

Mix the substance under examination with concentrated acetic acid to strongly acid reaction, and let the mixture digest for several hours. Then strain the fluid from the solid part, squeeze the latter, and wash it with water acidified with acetic acid; evaporate the whole of the fluid obtained to dryness on the water-bath. Boil the residue first with pure spirit of wine, then with spirit of wine containing some acetic acid; evaporate the solutions thus obtained nearly to dryness on the water-bath, dilute with water, add carbonate of soda to feebly alkaline reaction, evaporate to the consistence of syrup, and allow it to stand at rest for 24 hours; then dilute again with water, and filter the fluid from the precipitate formed; wash the latter with water, digest with concentrated

* *Otto*—"Instructions how to detect Poisons." The facts stated are fully borne out by the results of experiments made in my own laboratory.

acetic acid, dilute with water, and decolorize with pure blood charcoal. Examine the decolorized fluid in the usual way for the alkaloids. As the charcoal may retain alkaloids, do not omit examining it by the method given below, in 3.

3. METHOD OF EFFECTING THE DETECTION OF STRYCHNIA IN BEER, BY *Graham* AND *A. W. Hofmann.**

This method, which is based on the known fact that a solution of a salt of strychnia, when mixed and shaken with animal charcoal, yields its strychnia to the charcoal, will undoubtedly be found applicable also for the detection of other alkaloids. The process is conducted as follows :—

Shake 2 ounces of animal charcoal, with half-a-gallon of the aqueous neutral or feebly acid fluid under examination; let the mixture stand for from 12 to 24 hours, with occasional shaking, filter, wash the charcoal twice with water, and then boil for half-an-hour with 8 ounces of spirit of wine of 80—90 per cent., avoiding loss of alcohol by evaporation. Filter the spirit of wine hot from the charcoal, and distil the filtrate; add a few drops of solution of potassa to the residual watery fluid, shake with ether, let the mixture stand at rest, and then decant the supernatant ether. The ethereal fluid leaves, upon spontaneous evaporation, the strychnia in a sufficient state of purity to admit of its further examination by reagents (see § 235).

II.

GENERAL PLAN OF THE ORDER AND SUCCESSION IN WHICH SUBSTANCES SHOULD BE ANALYZED FOR PRACTICE.

It is not a matter of indifference whether the student, in analyzing for the sake of practice, follows no rule or order whatever in the selection of the substances which he intends to analyze, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways, indeed, may lead to the desired end, but one of them will invariably prove the shortest. I will, therefore, here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

Let the student take 100 compounds, systematically arranged (*see below*), and let him analyze these compounds successively in the order in which they are placed. A careful and diligent examination of these will be amply sufficient to impart to him the necessary degree of skill in practical analysis. When analyzing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed for him by a friend who knows their exact composition.

A. *From* 1 *to* 20.

AQUEOUS SOLUTIONS OF SIMPLE SALTS: *e. g.*, sulphate of soda, nitrate of lime, chloride of copper, &c. These investigations will serve to teach the student the method of analyzing substances soluble in water, which contain but one base. In these investigations it is only intended to

* "Chem. Soc. Quart. Journ.," V. 173.

ascertain which base is present in the fluid under examination; but neither the detection of the acid, nor the proof of the absence of all other bases besides the one detected, is required.

B. *From* 21 to 50.

SALTS, ETC., CONTAINING ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID (in form of powder): *e. g.*, carbonate of baryta, borate of soda, phosphate of lime, arsenites, chloride of sodium, bitartrate of potassa, acetate of copper, sulphate of baryta, chloride of lead, &c. These investigations will serve to teach the student how to make a preliminary examination of a solid substance, by heating in a tube or before the blowpipe; how to convert it into a proper form for analysis, *i.e.*, how to dissolve or decompose it; how to detect *one* metallic oxide, even in substances *insoluble* in water; and how to demonstrate the presence of *one* acid. The detection of both the base and the acid is required, but it is not necessary to prove that no other bodies are present.

C. *From* 51 *to* 65.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL BASES. These investigations will serve to teach the student the method of separating and distinguishing several metallic oxides from each other. The proof is required that no other bases are present besides those detected. No regard is paid to the acids.

D. *From* 66 to 80.

DRY MIXTURES OF EVERY DESCRIPTION. A portion of the salts should be organic, another inorganic; a portion of the compounds soluble in water or hydrochloric acid, another insoluble; *e. g.*, mixtures of chloride of sodium, carbonate of lime, and oxide of copper;—of phosphate of magnesia and ammonia, and arsenious acid;—of tartrate of lime, oxalate of lime, and sulphate of baryta;—of phosphate of soda, nitrate of ammonia, and acetate of potassa, &c.

These investigations will serve to teach the student how to treat mixtures of different substances with solvents; how to detect several acids in presence of each other; how to detect the bases in presence of phosphates of the alkaline earths;—and they will serve as a general introduction to scientific and practical analyses. All the component parts must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

NATIVE COMPOUNDS, ARTICLES OF COMMERCE, &c. Mineral and other waters, minerals of every description, soils, potash, soda, alloys, colors, &c.

III.

ARRANGEMENT OF THE RESULTS OF THE ANALYSES PERFORMED FOR PRACTICE.

The manner in which the results of analytical investigations ought to be arranged is not a matter of indifference. The following examples will serve to illustrate the method which I have found the most suitable in this respect.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 1—20.

Colorless fluid of neutral reaction.

HCl	HS	NH_4S	NH_4O, CO_2 and NH_4Cl
no precipitate, consequently no AgO Hg_2O	*no precipitate,* no PbO „ HgO „ CuO „ BiO_3 „ CdO	*no precipitate,* no FeO „ MnO „ NiO „ CoO „ ZnO	*a white precipitate,* consequently either BaO, SrO, or CaO, no precipitate by solution of sulphate of lime, consequently LIME.
	„ AsO_3 „ AsO_5 „ SbO_3 „ SnO_2 „ SnO „ AuO_3 „ PtO_2	„ Al_2O_3 „ Cr_2O_3	Confirmation by means of $\overline{O}$
	„ Fe_2O_3		

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 21—50.

White powder, fusing in the water of crystallization upon application of heat, and then remaining unaltered—soluble in water—reaction neutral.

HCl	HS	NH_4S	NH_4O, CO_2, and NH_4Cl	PO_5, $2NaO, HO$ and NH_4O
no precipitate.	*no precipitate.*	*no precipitate.*	*no precipitate.*	*a white precipitate,* consequently MAGNESIA.

The detected base being MgO, and the analyzed substance being soluble in water, Cl, I, Br, SO_3, NO_5, $\overline{A}$, &c., are the only acids or metalloids that can be present. The preliminary examination has proved the absence of the organic acids and of nitric acid.

Ba Cl produces a white precipitate which H Cl fails to dissolve; consequently SULPHURIC ACID.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, NOS. 51—100.

A white powder, acquiring a permanent yellow tint upon application of heat. Before the blowpipe, a ductile metallic globule, and yellow incrustation with white border upon cooling. Insoluble in water, effervescing with hydrochloric acid, incompletely soluble in that acid, readily soluble in nitric acid.

HCl	HS	NH_4S	NH_4O, CO_2	No fixed residue upon evaporation.	Hydrate of lime has failed to evolve ammonia.
White precipitate, insoluble in an excess of the precipitant, unaltered by ammonia: LEAD — confirmation by means of SO_3.	Black precipitate, insoluble in sulphide of ammonium, readily soluble in nitric acid. SO_3 produces a white precipitate: LEAD. Examination for Cu, Bi, and Cd, results negative.	White precipitate; ammonia, applied by itself, produces no precipitate; solution of precipitate in hydrochloric acid remains clear upon addition of soda in excess. NH_4Cl no precipitate. | HS white precipitate: ZINC.	White precipitate; upon dissolving this in hydrochloric acid, and adding solution of sulphate of lime to the fluid, a white precipitate forms after some time: STRONTIA. Precipitation with sulphate of potassa, filtrate tested for lime with $\bar{O}$, results negative.		

Of the acids, CARBONIC ACID has already been found. Of the remaining acids, the following cannot be present:

The preliminary examination has proved the absence of organic acids.

NO_5 and ClO_5, and also HCl, HI, and HBr, cannot be present, because the analyzed substance is insoluble in water.

S and SO_3 not, because the analyzed substance is readily soluble in nitric acid.

The white color of the analyzed compound proves the absence of CrO_3.

PO_5, SiO_2, HF, and $\bar{O}$ not, because the solution filtered from the sulphide of lead was not precipitated by simple addition of ammonia.

BO_3 might be present in trifling quantity; the examination for it gave a negative result.

The analyzed compound contains accordingly $\begin{cases}\text{bases: oxide of lead, oxide of zinc, strontia.}\\ \text{acids: carbonic acid.}\end{cases}$

IV.

TABLE

OF THE

MORE FREQUENTLY OCCURRING FORMS AND COMBINATIONS OF THE SUBSTANCES TREATED OF IN THE PRESENT WORK,

ARRANGED

WITH ESPECIAL REGARD TO THE CLASS TO WHICH THEY RESPECTIVELY BELONG ACCORDING TO THEIR SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, IN NITRIC ACID, OR IN NITROHYDROCHLORIC ACID.

PRELIMINARY REMARKS.

The class to which the several compounds respectively belong according to their solubility in water or acids (see § 177), is expressed by figures. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, nitric acid, or nitrohydrochloric acid; 3 or III a substance insoluble in water, in hydrochloric acid, and in nitric acid. For those substances which stand as it were on the limits between the various classes, the figures of the classes in question are jointly expressed: thus 1—2 signifies a substance difficultly soluble in water, but soluble in hydrochloric acid or nitric acid; 1—3 a body difficulty soluble in water, and of which the solubility is not increased by the addition of acids; and 2—3 a substance insoluble in water, and difficultly soluble in acids. Wherever the deportment of a substance with hydrochloric acid differs materially from that which it exhibits with nitric acid, this is stated in the notes.

The Roman figures denote officinal and more commonly occurring compounds.

The haloid salts and sulphur compounds are placed in the columns of the corresponding oxides. The salts given are, as a general rule, the neutral salts; the basic, acid, and double salts, if officinal, are mentioned in the notes; the small figures placed near the corresponding neutral or simple salts refer to these.

Cyanogen, chloric acid, citric acid, malic acid, benzoic acid, succinic acid, and formic acid, are of more common occurrence in combination with a few bases only, and have therefore been omitted from the table. The most frequently occurring compounds of these substances are: cyanide of potassium I, ferrocyanide of potassium I, ferricyanide of potassium I, sesqui-ferrocyanide of iron (Prussian blue) III, ferrocyanide of zinc and potassium II—III, chlorate of potassa I, the citrates of the alkalies I, the malates of the alkalies I, malate of sesquioxide of iron I, the benzoates of the alkalies I, the succinates of the alkalies I, and the formates of the alkalies I.

INDEX OF THE SOLUBILITY OF

	KO	NaO	NH_4O	BaO	SrO	CaO	MgO	Al_2O_3	MnO	FeO	Fe_2O_3	CoO	NiO	ZnO
	I	I	I	I	1	I-II	II	II	2	2	II	II	II	II
S	I	I	I	I	1	I-II	2		II	II	2	2_{15}	2_{16}	2
Cl	I	I	I_{12}	I	I	I	1	1	I	I	I_{12}	I	I	1
I	I	1	1	1	1	1	1		1	1	1			1
SO_3	I_1	I	I_{13}	III	III	I-III	I	$I_{1 \cdot 13}$	I	I	I	1	I	I
NO_5	I	I	I	I	I	1	1	1	1	1	1	I	1	1
PO_5	1	I_{10}	1_{10}	2	2	II_{14}	2		2	2	II	2	2	2
CO_2	I_2	I_{11}	I	II	II	II	II		II	II		2	2	II
C_2O_3	I_3	1	I	2	2	II	2	2	2	1-2	1-2	2		2
BO_3	1_4	I_4	1	2	2	2	2	2	2	2	2	2	2	2
$\overline{A}$	I	I	I	I	1	I	1	1	1	1	I	1	1	I
$\overline{T}$	$I_{4 \cdot 9}$	I_7	1_6	2	2	II	1-2	1	1-2	1-2	I_8	1		2
AsO_5	I	1	1	2	2	2	2	2	2	2	2	2	2	
AsO_3	I	1	1	2	2	2				2		2	2	
CrO_3	I	1	1	2	2	2	1	2	1		1	2	2	1

NOTES.

1. SULPHATE of potassa and alumina I.
2. Bicarbonate of potassa I.
3. Binoxalate of potassa I.
4. Tartarized borax (bitartrate of potassa and borate of soda) I.
5. Bitartrate of potassa I-II.
6. Tartrate of potassa and ammonia I.
7. Tartrate of potassa and soda I.
8. Tartrate of potassa and sesquioxide of iron I.
9. Tartrate of antimony and potassa I.
10. Phosphate of soda and ammonia I.
11. Bicarbonate of soda I.
12. Sesquichloride of iron and chloride of ammonium I.
13. Sulphate of alumina and ammonia I.
14. Basic phosphate of lime II.
15. Sulphide of cobalt is pretty readily decomposed by nitric acid, but very difficultly by hydrochloric acid. This substance is not officinal.

SUBSTANCES IN WATER OR ACIDS.

	CdO	PbO	SnO	SnO_2	BiO_3	CuO	Hg_2O	HgO	AgO	PtO_2	AuO_3	SbO_3	Cr_2O_3
	2	II_{18}	2	2 & 3	2	II_{22}	II	II	2	2		$_{35}$	II & III
S	2	II	2_{20}	2_{20}	2	2_{23}	II	II	2_{30}	2_{31}		II_{36}	
Cl	1	I-III	I	1	I	I_{24}	II-III	I_{28}	III	$I_{32\cdot 33}$	I_{34}	I_{37}	I & III
I	1	I-II	2	1			II	II	3				
SO_3	I	II-III	1		1	I_{25}	1-2	1_{29}	I-II	1		2	I & III
NO_5	1	I			I_{21}	I	I_{27}	I	I	1			I
PO_5	2	2				2	2	2	2				2
CO_2	2	II			2	II	2	2	2				
C_2O_3	2	2	2	1	2	2	2	2	2			1-2	1
BO_3	1-2	2	2		2	2	1						2
$\overline{A}$	1	I_{19}	1	1	1	I_{26}	1-2	1	1			1	1
$\overline{T}$	1-2	2	1-2		2	1	1-2	2	2			I_{38}	1
AsO_5		2			2	2	2	2	2			2	2
AsO_3		2				II	2	2	2			2	
CrO_3		II-III	2		2	2	2	1-2	2			2	2

16. The same applies to sulphide of nickel.
17. Sulphide of zinc is readily soluble in nitric acid, somewhat more difficultly soluble in hydrochloric acid.
18. Minium is converted by hydrochloric acid into chloride of lead; by nitric acid into oxide, which redissolves in an excess of the acid, and into brown binoxide of lead, which is insoluble in nitric acid.
19. Trisacetate of lead I.
20. Proto- and bisulphide of tin are decomposed and dissolved by hydrochloric acid; by nitric acid they are converted into binoxide, which is insoluble in an excess of the acid. Sublimed bisulphide of tin dissolves only in nitrohydrochloric acid.
21. Basic nitrate of teroxide of bismuth II.
22. Ammoniated oxide of copper 1.
23. Sulphide of copper is difficultly decomposed by hydrochloric acid, but with facility by nitric acid.
24. Chloride of copper and ammonium I.
25. Sulphate of copper and ammonia I.

26. Basic acetate of copper, partially soluble in water, and completely in acids.
27. Basic nitrate of suboxide of mercury and ammonia II.
28. Ammonio-chloride of mercury II.
29. Basic sulphate of oxide of mercury II.
30. Sulphide of silver soluble only in nitric acid.
31. Bisulphide of platinum is not affected by hydrochloric acid, and but little by boiling nitric acid; it dissolves in hot nitrohydrochloric acid.
32. Bichloride of platinum and chloride of potassium 1—3.
33. Bichloride of platinum and chloride of ammonium 1—3.
34. Terchloride of gold and chloride of sodium I.
35. Teroxide of antimony is soluble in hydrochloric acid, but not in nitric acid.
36. Tersulphide of antimony and sulphide of calcium I—II.
37. Basic terchloride of antimony II.
38. Tartrate of teroxide of antimony and potassa I.

V.

TABLE OF WEIGHTS AND MEASURES.

GRAMMES.		GRAINS.	DECIGRAMMES.		GRAINS.
1	=	15·4346	1	=	1·5434
2	...	30·8692	2	...	3·0869
3	...	46·3038	3	...	4·6304
4	...	61·7384	4	...	6·1738
5	...	77·1730	5	...	7·7173
6	...	92·6076	6	...	9·2607
7	...	108·0422	7	...	10·8042
8	...	123·4768	8	...	12·3476
9	...	138·9114	9	...	13·8911

CENTIGRAMMES.		GRAINS.	MILLIGRAMMES.		GRAINS.
1	=	·1543	1	=	·0154
2	...	·3086	2	...	·0308
3	...	·4630	3	...	·0463
4	...	·6173	4	...	·0617
5	...	·7717	5	...	·0771
6	...	·9260	6	...	·0926
7	...	1·0804	7	...	·1080
8	...	1·2347	8	...	·1234
9	...	1·3891	9	...	·1389

METRES.		INCHES.	DECIMETRES.		INCHES.
1	=	39·37	1	=	3·937
2	...	78·74	2	...	7·874
3	...	118·11	3	...	11·811
4	...	157·48	4	...	15·748
5	...	196·85	5	...	19·685
6	...	236·22	6	...	23·622
7	...	275·59	7	...	27·559
8	...	314·96	8	...	31·496
9	...	354·33	9	...	35·433

CENTIMETRES.		INCHES.	MILLIMETRES.		INCHES.
1	=	·3937	1	=	·03937
2	...	·7874	2	...	·07874
3	...	1·1811	3	...	·11811
4	...	1·5748	4	...	·15748
5	...	1·9685	5	...	·19685
6	...	2·3622	6	...	·23622
7	...	2·7559	7	...	·27559
8	...	3·1496	8	...	·31496
9	...	3·5433	9	...	·35433

One kilogramme	=	15434 grains.
One cubic centimetre	=	0·0610 cubic inch.
One litre	=	61·0271 cubic inches.

ALPHABETICAL INDEX.

THE END.

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